Hydrotreating Process, Environment Friendly Gasoline Base Oil and Unleaded Gasoline Composition

[Field of the Invention]

The present invention relates to a process for hydrotreating a feedstock containing a fat component originating from an animal or vegetable oil and an environment friendly gasoline base oil produced by the process. Further, the present invention also relates to an unleaded gasoline composition containing the environment friendly gasoline base oil, which composition is excellent in exhaust gas purifying properties, fuel consumption and drivability.

[Background of the Invention]

Conventionally, gasoline has been produced by blending one or more types of base gasoline fractions produced by processing crude oil in various refining units such as a catalytic reformer or a catalytic cracker (see, for example, Non-Patent Document No. 1).

Recently, an automobile has been required to reduce harmful substances contained in the exhaust gas for improving the atmospheric environment and to reduce the emissions of CO_2 which is a gas causing the greenhouse effect in view of global warming prevention.

A gasoline-powered automobile is extremely low in the amount of harmful substances in the exhaust gas but has been required to reduce the CO_2 emissions by improving thermal efficiency and fuel consumption. In the mid- and long-terms, the diversification of sources of fuels for transportation purposes and the establishment of sustainable mobility have been demanded.

Under these circumstances, an attention has been drawn to the use of a biomass-originating fuel, which is capable of preventing life cycle CO_2 emissions from increasing, contributive to the diversification of sources of fuels, and reproducible, as a fuel for gasoline-powered automobiles. Among biomass energies, those originating from vegetables in particular can make effectively the use of hydrocarbons converted from carbon dioxide by photosynthesis through the growth process of vegetables and thus have the so-called carbon neutral characteristics, which do not lead to an increase in carbon dioxide in the atmosphere in view of the life cycle. If these biomass energies such as fuels originating from animals or vegetable oils can be used as gasoline fuel, it is expected to play an effective role for decreasing reducing carbon dioxide emissions in view of the fact that gasoline engines have been broadly used.

Examples of known biomass-originating base oils, which can be blended with gasoline include ethanol (biomass-originating ethanol) produced by fermenting a sugar component mainly containing starch of sugar cane or corn, and ETBE (ether tertially-butyl ether) produced by reacting the biomass-originating ethanol with isobutylene produced by separating mixed butylene produced in a fluid catalytic cracker (FCC) in a refinery or a steam cracker in an ethylene plant (see, for example, Non-Patent Document No. 2).

It has been studied to use a fatty acid alkyl ester mixture produced from a natural animal or vegetable fat, alone or in combination with an existing gas oil, as a fuel for diesel-powered automobiles (see, for example, Non-Patent Document No. 3). However, since the gasoline engine and the diesel engine are different from one another in ignitability and distillation range, required for their fuels, it is difficult to use such a fatty acid methyl ester originating from an animal or vegetable oil as a fuel for gasoline-powered automobiles. Further, the fatty acid methyl eater oil is produced by ester-exchange of the triglyceride structure that is a common structure for animal or vegetable oils, with methanol using alkalis. However, as described in Patent Document No. 1 below, it has been

pointed out that the process of producing a fatty acid methyl eater oil requires disposal of glycerin formed as a by-product and that washing the produced oil is cost- and energy-consuming.

(1) Patent Document No.1: Japanese Patent Application Laid-Open Publication No. 2005-154647

(2) Non-Patent Document No. 1: "Shinhan Nenryou Binran" edited by The Fuel Society of Japan, published by CORONA PUBLISHING CO., LTD., in March 1974, pp 264-267

(3) Non-Patent Document No. 2: Material No. 3 delivered at the 3rd Council on the Promotion of the Use of Renewable Fuels (October 10, 2003) hosted by Ministry of the Environment

(4) Non-Patent Document No. 3: 7th Report of the Central Environment Council, July 29, 2003

[Disclosure of the Invention]

In addition to the aforesaid problems, the use of animal or vegetable fat components or fuels produced therefrom arises the following problems. That is, since fat components originating from animal or vegetable oils generally contain oxygen in their molecules, oxygen components would adversely affect

materials forming an engine and it is difficult to reduce the oxygen components to an extremely low concentration. When a fat component originating from an animal or vegetable oil is mixed with a petroleum hydrocarbon fraction, it is impossible to reduce sufficiently both the oxygen content in the fat component and the sulfur content in the petroleum hydrocarbon fraction with the conventional techniques. Further, when the fat component is used as a fuel base oil, it is preferably less in normal paraffin content and more in isoparaffin content. For an automobile gasoline, for example, higher normal paraffin content causes insufficient octane number.

Therefore, the present invention has an object to provide a process for hydrotreating a feedstock enabling the production of a hydrotreated oil which is sufficiently reduced in oxygen and sulfur contents and sufficiently less in normal paraffin content when using the feedstock containing an oxygen-containing hydrocarbon compound or further containing a sulfur-containing compound, an environment friendly gasoline base oil produced by the process and an unleaded gasoline composition containing the environment friendly gasoline base oil.

That is, the present invention provides a process

for hydrotreating a feedstock, comprising bringing the feedstock into contact with a catalyst in the presence of hydrogen, the feedstock containing an oxygen-containing compound, the catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Group 8 elements of the periodic table.

The present invention provides a process for hydrotreating a feedstock, comprising bringing the feedstock into contact with a catalyst in the presence of hydrogen, the feedstock containing an oxygen-containing compound and a sulfur-containing compound, the catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Groups 6A and 8 elements of the periodic table.

According to the present invention, a hydrotreated oil which is sufficiently reduced in oxygen and sulfur contents and sufficiently less in normal paraffin content can be produced in an economically efficient manner by bringing a feedstock containing an oxygen-containing compound into contact with a specific catalyst.

In the hydrotreating processes of the present invention, the feedstock is preferably contacted with

the catalyst under such conditions that the oxygen content and normal paraffin content of the fraction in a boiling point range of 80 to 135°C of the resulting hydrotreated oil are 0.2 percent by mass or less and 30 percent by mass or less, respectively. Hydrotreating of the feedstock under these conditions enables the production of a hydrotreated oil containing higher level of components effective as a gasoline base oil. In this case, the processes enable the economically efficient production of an environment friendly gasoline base oil which is sufficiently reduced in oxygen and sulfur contents and sufficiently less in normal paraffin content.

In the hydrotreating process of the present invention, when a feedstock containing an oxygen-containing hydrocarbon compound is contacted with a catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Group 8 elements of the periodic table, the oxygen and sulfur contents of the feedstock are preferably from 0.1 to 15 percent by mass and 50 ppm by mass or less, respectively on the basis of the total mass of the feedstock. When the oxygen and sulfur contents of the feedstock are within the above ranges, stable deoxidization activity can be

maintained for a long period of time.

In the hydrotreating process of the present invention, when a feedstock containing an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound is contacted with a catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Groups 6A and 8 elements of the periodic table, the oxygen and sulfur contents of the feedstock are preferably from 0.1 to 15 percent by mass and from 1 ppm by mass to 1 percent by mass, respectively on the basis of the total mass of the feedstock. When the oxygen and sulfur contents of the feedstock are within the above ranges, stable deoxidization activity can be maintained for a long period of time.

In the hydrotreating process of the present invention, the oxygen-containing hydrocarbon compound is preferably a fat component originating from an animal or vegetable oil with the objective of using biomass energy efficiently.

The ratio of the compound having a triglyceride structure in the oxygen-containing hydrocarbon compound is preferably 90 percent by mole or more with the objective of reducing the energy required for

processing raw materials.

In the hydrotreating process of the present invention, the Group 8 elements contained in the catalyst are preferably one or more metals selected from Pd, Pt, Rh, Ir, Au and Ni.

In the hydrotreating process of the present invention, the Group 6A and 8 elements contained in the catalyst are preferably one or more metals selected from Co, Mo and Ni.

In the hydrotreating process of the present invention, the crystalline metallosilicate contained in the catalyst preferably has a structure of faujasite type.

Further, the crystalline metallosilicate is preferably an ultra-stable Y type zeolite having a molar ratio of the silica to the alumina (silica/alumina) within the range of 10 to 100. When the molar ratio is less than 10, the formation of coke would be facilitated, possibly resulting in a significant reduction in activity. When the molar ratio is in excess of 100, hydrotreating activity would be insufficient, resulting in the likelihood that the yield of components useful for a fuel base oil would be reduced.

According to the present invention, there is also

provided an environment friendly gasoline base oil comprising a fraction with a boiling point range of 25 to 220°C of the hydrotreated oil produced by the foregoing hydrotreating process of the present invention.

The environment friendly gasoline base oil preferably has an oxygen content of 0.2 percent by mass or less and a normal paraffin content of 30 percent by mass or less.

Further, the present invention also provides an unleaded gasoline composition comprising the aforesaid environment friendly gasoline base oil. The unleaded gasoline composition comprising the aforesaid environment friendly gasoline base oil of the present invention can accomplish a reduction in carbon dioxide emissions effectively.

The unleaded gasoline composition of the present invention is preferably an unleaded gasoline with a research octane number of 89.0 or greater and less than 96.0 and a sulfur content of 10 ppm by mass or less or an unleaded gasoline with a research octane number of 96.0 or greater and a sulfur content of 10 ppm by mass or less.

Preferably, the unleaded gasoline composition of the present invention has a 10% distillation

temperature of 70°C or lower, a 50% distillation temperature of 75°C or higher and 110°C or lower, a 90% distillation temperature of 180°C or lower, an end point of 220°C or lower, a vapor pressure (37.8°C) of 44 kPa or greater and 93 kPa or less, a density (15°C) of 0.783 g/cm^3 or less, an oxidation stability of 240 minutes or longer, a copper corrosion (50°C, 3 hours) of 1 or less, a washed existent gum content of 5 mg/100 ml or less, an unwashed existent gum content of 20 mg/100 ml or less and a benzene content of 1 percent by volume or less.

Preferably, the unleaded gasoline composition of the present invention has an aromatic content of 45 percent by volume or less and an olefin content of 35 percent by volume or less.

Preferably, the unleaded gasoline composition of the present invention has a manganese content of 2 ppm by mass or less, an iron content of 2 ppm by mass or less, a sodium content of 2 ppm by mass or less, a potassium content of 2 ppm by mass or less and a phosphorus content of 2 ppm by mass or less.

Preferably, the unleaded gasoline composition of the present invention contains an anti-oxidant and a metal deactivator or contains a detergent-dispersant and a friction modifier.

[Effects of the Present Invention]

According to the present invention, there is provided a process of hydrotreating a feedstock enabling the production of a hydrotreated oil which is sufficiently reduced in oxygen and sulfur contents and sufficiently less in normal paraffin content in an extremely economically efficient manner when using a feedstock containing an oxygen-containing hydrocarbon compound and alternatively further containing a sulfur-containing hydrocarbon compound. Further, according to the present invention, there is provided an environment friendly gasoline base oil and an unleaded gasoline composition, which can efficiently accomplish a reduction in carbon dioxide emissions.

[Best Mode of Carrying out the Invention]

The present invention will be described in more detail below.

A feedstock containing an oxygen-containing hydrocarbon compound or a feedstock further containing a sulfur-containing hydrocarbon compound is used in the present invention. The oxygen-containing hydrocarbon compound is suitably an animal or vegetable-originating fat component that is biomass.

The fat component used herein incorporates naturally or artificially made or produced animal or vegetable fats, animal or vegetable fat components and/or components made or produced from these fats, and components to be added for the purpose of maintaining and improving the properties of the fat products.

Examples of the fat components originating from animal or vegetable oils include vegetable oils such as rapeseed oil, corn oil, soy bean oil, grape seed oil and palm oil and animal oils such as beef tallow and lard. Any fat may be used as the fat component originating from animal or vegetable oils in the present invention. Alternatively, waste oils resulting from the use of these fats may be used. However, in view of carbon neutral, it is preferable to use vegetable fats, and in view of the carbon number of the fatty acid alkyl chain and reactivity thereof, it is more preferable to use rapeseed oil, soy bean oil and palm oil. The foregoing fats may be used alone or in combination.

In general, the fat components originating from animal or vegetable oils have a fatty acid triglyceride structure but may contain other fatty acids or fat components modified to an ester, such as fatty acid methyl ester. However, the vegetable fat preferably

contains mainly a component having a triglyceride structure with the objective of reducing carbon dioxide emissions because carbon dioxide is generated upon production of fatty acids or fatty acid esters from vegetable fats. In the present invention, the ratio of the compound having a triglyceride structure in the oxygen-containing hydrocarbon compound contained in the feedstock is preferably 90 percent by mole or more, more preferably 92 percent by mole or more, more preferably 95 percent by mole or more.

The oxygen content of the feedstock is preferably from 0.1 to 15 percent by mass, more preferably from 1 to 15 percent by mass, more preferably from 3 to 14 percent by mass, particularly preferably from 5 to 13 percent by mass on the basis of the total mass of the feedstock. If the oxygen content is less than 0.1 percent by mass, it would be difficult to maintain stable deoxidization and desulfurization activities. Whereas, the oxygen content is in excess of 15 percent by mass, there may arise the necessity of facilities for disposal of by-produced water or water and the catalyst support would be excessively interacted, resulting in a reduction in activity or catalyst strength. The oxygen content can be measured with a conventional elemental analysis device. For example,

the oxygen content is measured by converting a sample on platinum carbon to carbon monoxide or further to carbon dioxide and measuring the amount thereof using a thermal conductivity detector.

In the present invention, the feedstock may contain a sulfur-containing hydrocarbon compound. There is no particular restriction on the sulfur-containing hydrocarbon compound. Examples thereof include sulfide, disulfide, polysulfide, thiol, thiophene, benzothiophene, dibenzothiophene, and derivatives thereof. The sulfur-containing hydrocarbon compound contained in the feedstock may be a single compound or a mixture of two or more types of these compounds. Alternatively, a petroleum hydrocarbon fraction containing sulfur may be used as the sulfur-containing hydrocarbon compound.

The petroleum hydrocarbon fraction may be a fraction produced through general petroleum-refining processes. For example, the fraction may be a fraction within a predetermined boiling point range produced from an atmospheric distillation unit or a vacuum distillation unit or a fraction within a predetermined boiling point range produced from a hydrodesulfurization unit, a hydrocracking unit, a residue direct hydrodesulfurization unit or a fluid

catalytic cracking unit. The fraction produced from each of these units may be used alone or in combination.

Further, the feedstock may contain compounds originating from chemical products such as plastics or solvent and may contain a synthetic oil produced through a Fischer–Tropsch reaction using a feedstock which is a synthetic gas composed of carbon monoxide and hydrogen.

When the feedstock containing an oxygen-containing hydrocarbon compound is contacted with a catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Group 8 elements of the periodic table, in the hydrotreatment process of the present invention, the sulfur content of the feedstock is preferably 50 ppm by mass or less on the basis of the total mass of the feedstock. If the sulfur content is in excess of 50 ppm by mass, the hydrotreated oil is likely to be increased in sulfur content and thus would adversely affect the exhaust gas purification device of a gasoline engine when it is used therefor. When the feedstock containing an oxygen-containing hydrocarbon compound and a sulfur-containing hydrocarbon compound is contacted with a catalyst comprising a support containing a crystalline

metallosilicate and one or more types of metals selected from the Groups 6A and 8 elements of the periodic table, the sulfur content of the feedstock is preferably from 1 ppm by mass to 1 percent by mass, more preferably from 15 ppm by mass to 0.5 percent by mass, more preferably from 30 ppm by mass to 0.1 percent by mass on the basis of the total mass of the feedstock. If the sulfur content is less than 1 ppm by mass, it would be difficult to maintain stable deoxidization activity. If the sulfur content is in excess of 1 percent by mass, the hydrotreated oil is likely to be increased in sulfur content and thus would adversely affect the exhaust gas purification device of a diesel engine when it is used therefor. The sulfur content used herein denotes the mass content of sulfur measured in accordance with JIS K 2541 "Crude oil and petroleum products-Determination of sulfur content" or the method described in ASTM-5453.

The sulfur-containing hydrocarbon compound may be mixed with the feedstock beforehand and then introduced into the reactor of a hydrotreating unit or alternatively may be supplied to a section before the reactor when the feedstock is introduced therein.

The feedstock used in the present invention preferably contains a fraction with a boiling point of

300°C or higher and does not contain a heavy fraction with a boiling point of higher than 700°C. When a feedstock not containing a fraction with a boiling point of 300°C or higher is used, it would be difficult to obtain a sufficient yield because excess decomposition may occur. Whereas, when a feedstock containing a heavy fraction with a boiling point of higher than 700°C is used, heavy components would accelerate precipitation of carbon in the catalyst, possibly resulting in a reduction in activity. The boiling point used herein denotes the value measured in accordance with JIS K 2254 "Petroleum products-Determination of distillation characteristics" or the method described in ASTM-D86.

The present invention provides a first hydrotreating process (hereinafter referred to as "hydrotreatment A") wherein a feedstock containing an oxygen-containing hydrocarbon is contacted in the presence of hydrogen with a catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Group 8 elements of the periodic table to be hydrotreated.

The present invention also provides a second hydrotreating process (hereinafter referred to as "hydrotreatment B") wherein a feedstock containing an

oxygen-containing hydrocarbon and a sulfur-containing hydrocarbon compound is contacted with a catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Groups 6A and 8 elements of the periodic table to be hydrotreated.

The supports of the catalysts used in the present invention are porous inorganic oxides having a crystalline metallosilicate. The crystalline metallosilicate has a structure represented by a code preferably such as FAU, AEL, MFI, MMW, TON, MTW, *BEA, and MOR, more preferably FAU, *BEA, MOR or MFI defined by International Zeolite Association. In the present invention, the metallosilicate has more preferably a structure represented by FAU also referred to as "faujasite type". Further, the metallosilicate is particularly preferably of Y-type have been ultra-stabilized. The ultra-stabilization indicates a hydrothermal treatment and/or a washing treatment with an acid solution and can provide the resulting catalyst with a pore volume which is defined as mesopore which must have a pore diameter of 2 to 50 nm by adjusting the content of aluminum if contained in the structure.

The metallosilicate contained in the support of the catalyst used in the present invention is

preferably a crystalline aluminosilicate composed of three elements, i.e., aluminum, silicon and oxygen. The crystalline aluminosilicate may be the so-called zeolite containing silica and alumina. Preferable examples include Y-type zeolite, ultra stable Y-type zeolite (USY-type zeolite), β-type zeolite, mordenite and ZSM-5. Among these zeolites, particularly preferred is USY zeolite. In the present invention, these crystalline aluminosilicates may be used alone or in combination.

When the crystalline metallosilicate contains silica and alumina, the molar ratio of the silica to the alumina (silica/alumina) is preferably within the range of 10 to 100. The molar ratio is less than 10, the formation of coke would be accelerated and would invite a reduction in activity. When the molar ratio is in excess of 100, hydrotreating activity would be insufficient, possibly resulting in a reduction in the yield of components useful as a fuel base oil. In the present invention, the support of the catalyst preferably contains the crystalline metallosilicate that is an ultra-stable Y-type zeolite with a molar ratio of the silica to the alumina (silica/alumina) is within the range of 10 to 100.

There is no particular restriction on the method

of synthesizing the crystalline metallosilicate. Any conventional method may be used. For example, the crystalline metallosilicate may be synthesized by heating raw materials of constituting components if necessary in the coexistence of a structural indicator. Examples of the raw materials include silicon-containing compounds such as sodium silicate, colloidal silica, and alkoxide silicate and aluminum-containing compounds such as aluminum oxide and sodium aluminate. Examples of the structural indicator include amine compounds such as tetrapropyl ammonium salt.

The catalyst used in the present invention may contain constituting components other than the above-described crystalline metallosilicate. Examples of constituting components other than the above-described crystalline metallosilicate include inorganic oxides containing elements selected from aluminum, silicon, zirconium, boron, titanium and magnesium. These inorganic oxides function as a binder for shaping the crystalline metallosilicate and also as an active components for facilitating hydrodeoxidization and hydroisomerization. The inorganic oxides are preferably those containing two or more types of elements selected from aluminum,

silicon, zirconium, boron, titanium and magnesium with the objective of ensuring the above-described functions.

The content of the metallosilicate in the whole catalyst is preferably from 2 to 90 percent by mass, more preferably from 5 to 85 percent by mass, more preferably from 10 to 80 percent by mass. When the metallosilicate content is less than 2 percent by mass, the hydrodeoxidization and hydroisomerization activities of the resulting catalyst would likely be insufficient. When the content is in excess of 90 percent by mass, the moldability of the catalyst would be too low, rendering it difficult to produce the catalyst on commercial basis.

In hydrotreatment A, the catalyst is used, which comprises one or more types of metals selected from the Group 8 elements of the periodic table, supported on the above-described porous inorganic oxide support. Among these metals, preferred are one or more metals selected from Pd, Pt, Rh, Ir, Au, and Ni. When two or more metals are used in combination, preferred combinations are 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, Pd-Pt-Rh, Pd-Pt-Ir, and Pt-Pd-Ni. Among these combinations, more preferred are Pd-Pt, Pd-Ni,

Pt-Ni, Pd-Ir, Pt-Rh, Pt-Ir, Rh-Ir, Pd-Pt-Rh, Pd-Pt-Ni, and Pd-Pt-Ir. Further more preferred are Pd-Pt, Pd-Ni, Pt-Ni, Pd-Ir, Pt-Ir, Pd-Pt-Ni, and Pd-Pt-Ir. Upon hydrotreatment, these metals are preferably used after being converted to reductants.

With regard to the content of the active metal(s) on the basis of the catalyst mass, the total content of metals selected from the Group 8 elements of the periodic table is preferably from 0.1 to 2 percent by mass, more preferably from 0.2 to 1.5 percent by mass, more preferably from 0.5 to 1.3 percent by mass. If the total content is less than 0.1 percent, the active sites are reduced, leading to a tendency that a sufficient activity may not be attained. If the total content is more than 2 percent by mass, the metals are not dispersed effectively, leading to a tendency that a sufficient activity may not be attained.

In hydrotreatment B, the catalyst is used, which comprises one or more types of metals selected from the Groups 6A and 8 elements of the periodic table, supported on the above-described porous inorganic oxide support. Among these metals, one or more types of metals selected from Co, Mo and Ni are preferably supported. Two or more metals selected from Co, Mo and Ni are preferably supported in combination.

Preferable combinations are Co-Mo, Ni-Mo and Ni-Co-Mo. At least one or more types selected from the Group 6A elements of the periodic table are preferably supported on the above-described porous inorganic oxide. Upon hydrotreatment, these metals are preferably used after being converted to reductants.

When one or more types of metals selected from Co, Mo and Ni are supported, the total content of the active metal(s) is preferably from 15 to 35 percent by mass, more preferably from 17 to 30 percent by mass on the basis of the mass of the catalyst. If the total content is less than 15 percent, the active sites are reduced, leading to a tendency that a sufficient activity may not be attained. If the total content is more than 35 percent by mass, the metals are not dispersed effectively, leading to a tendency that a sufficient activity may not be attained. With regard to the contents of Co, Mo, and Ni, those in terms of oxide are used herein.

There is no particular restriction on the method of supporting the active metals on the catalysts. Therefore, any conventional method for producing a usual desulfurization catalyst may be employed. A method is preferably employed in which a support is impregnated with a solution containing salts of the

active metals. Alternatively, an equilibrium adsorption method, pore-filling method, or incipient-wetness method is also preferably used. For example, the pore-filling method is a method in which the pore volume of a support is measured in advance, and then the support is impregnated with the same volume of a metal salt solution. There is no particular restriction on the method of impregnating the support with a solution. Therefore, any suitable method may be used depending on the amount of the metals to be supported and physical properties of the support.

There is no particular restriction on the number of type of hydrotreatment catalyst in each hydrotreatment A and B of the present invention. For example, one type of catalyst may be used alone, or a plurality of catalysts each having different active metal or support-constituting components may be used. When a plurality of catalysts each having a different support component are used in combination, , a catalyst with a metallosilicate content within the range of 2 to 90 percent by mass may be used in a stage after a catalyst with a metallosilicate content of 5 percent by mass or less, both contents being on the basis of the total mass of the support.

If necessary, in addition to the hydrotreatment

catalysts, a guard catalyst, a demetallization catalyst, and an inert filler may be used alone or in combination for the purposes of trapping scale fractions flowing into the reactor, accompanied with the feedstock and supporting the hydrotreatment catalysts at portions segmenting the catalyst beds.

Conditions under which the feedstock is contacted with the catalysts in the presence of hydrogen are a hydrogen pressure of 2 to 13 MPa, a liquid hourly space velocity (LHSV) of 0.1 to 3.0 h^{-1} and a hydrogen oil pressure (hydrogen/oil ratio) of 150 to 1500 NL/L, preferably a hydrogen pressure of 2 to 10 MPa, a liquid hourly space velocity of 0.2 to 2.0 h^{-1} and a hydrogen oil ratio of 200 to 1200 NL/L, more preferably a hydrogen pressure of 2 to 6 MPa, a liquid hourly space velocity of 0.3 to 1.5 h^{-1} and a hydrogen oil ratio of 250 to 1000 NL/L. Each of the conditions is a factor exerting an influence on the reaction activity. For example, if the hydrogen pressure and hydrogen/oil ratio are less than the lower limits, the reactivity tends to reduce, and the activity tends to reduce rapidly. If the hydrogen pressure and hydrogen/oil ratio exceed the upper limits, an enormous plant investment for a compressor may be required. Lower liquid hourly space velocity tends to be more advantageous for the

reactions. However, if the liquid hourly space velocity is lower than the lower limit, an enormous plant investment for construction of a reactor with an extremely large volume may be required. If the liquid hourly space velocity exceeds the upper limit, the reaction tends to proceed insufficiently. The reaction temperature is preferably from 250 to 550°C, more preferably from 280 to 480°C, more preferably from 300 to 460°C.

The reactor may be of a fixed bed mode. That is, supply of hydrogen to the feedstock may be carried out in the form of counter flow or parallel flow. Alternatively, counter flow and parallel flow may be combined in a plurality of reactors. The supply mode of the feedstock is generally down flow. Gas-liquid cocurrent flow may be employed. The reactor may be a single reactor or a combination of a plurality of reactors. A single reactor with the interior segmented into a plurality of catalyst beds may also be employed.

The feedstock hydrotreated in a reactor is fractionated into hydrotreated oils each containing a predetermined fraction through gas-liquid separation and rectification. For example, the hydrotreated feedstock is fractionated into a gas oil fraction or a residue fraction. If necessary, the hydrotreated

feedstock may be often fractionated into gas, a naphtha fraction and a kerosene fraction. There is the possibility that water, carbon monoxide, carbon dioxide and hydrogen sulfide may be generated, accompanied with the reaction of oxygen or sulfur components contained in the feedstock. Therefore, a gas-liquid separation device or any other by-produced gas removal device may be installed between the plurality of reactors or in the product recovering step.

Hydrogen is generally introduced into a first reactor via its inlet, accompanying the feedstock, before or after the feedstock passes through a heating furnace. Alternatively, hydrogen gas may be introduced from the spaces between the catalyst beds or between a plurality of reactors for the purposes of controlling the temperature in the reactors and maintaining the hydrogen pressure over the whole reactors. Hydrogen to be introduced in such a manner is referred to as "quenching hydrogen". The ratio of the quenching hydrogen to the hydrogen introduced, accompanying the feedstock is preferably from 10 to 60 percent by volume, more preferably from 15 to 50 percent by volume. The ratio of less than 10 percent by volume would cause a tendency that the reaction at reaction

sites in the subsequent stages does not proceed sufficiently. The ratio in excess of 60 percent by volume would cause a tendency that the reaction near the inlet of the reactor does not proceed sufficiently.

The kerosene fraction and/or gas oil fraction and/or residue produced by the hydrotreatment of the present invention may be recycled by being mixed with the feedstock in whole or part thereby increasing the yield of a gasoline fraction.

In the hydrotreatment process of the present invention, the base oil composed of the whole or part of a fraction with a distillation temperature range of 25 to 220°C has preferably an oxygen content of 0.2 percent by mass or less and a normal paraffin content of 30 percent by mass or less. Further, the feedstock is preferably hydrotreated under such conditions that the fraction has an oxygen content of 0.2 percent by mass or less and a normal paraffin content of 25 percent by mass or less. In the hydrotreated oil produced by the hydrotreatment process of the present invention, the remaining oxygen components are present in the form of any of functional groups such as hydroxyl group, aldehyde group or carboxyl group or a plurality of the functional groups. However, if the oxygen content of the fraction is in excess of 0.2 percent by mass,

corrosivity would be high and the aldehyde concentration in the exhaust gas would be increased. If the normal paraffin content of the fraction is in excess of 30 percent by mass, the octane number of the resulting gasoline base oil would be decreased, and thus the resulting gasoline product would be poor in anti-knocking properties during high speed driving. Among the conditions under which the feedstock is contacted with the catalyst to satisfy the above requirements of the hydrotreated oil, the reaction temperature and liquid hourly space velocity are preferably adjusted for the hydrotreatment thereby producing a component useful as a gasoline base oil from the feedstock. The normal paraffin content used herein can be measured in accordance with JIS K2536-2 "Liquid petroleum products-Testing method of components part 2: Determination of total components by gas chromatography".

The hydrotreated oil comprising the whole or part of a fraction with a distillation temperature range of 25 to 220°C produced by the present invention is preferably used as a gasoline base oil. The unleaded gasoline composition of the present invention (may be hereinafter referred to as "the gasoline of the present invention") comprises the gasoline base oil (may be

hereinafter referred to as "the environment friendly gasoline base oil of the present invention").

Examples of the fraction range include a 25 to 70°C light fraction, a 70 to 160°C middle fraction, and a 160 to 220°C heavy fraction. Other than these fractions, there may be used a remaining fraction produced by removing a part of fraction with a specific distillation temperature range from a 25 to 220°C fraction.

In view of octane number, the fraction is preferably a light fraction. More specifically, the fraction is a light fraction with a distillation temperature of preferably 150°C or lower, more preferably 120°C or lower, more preferably 100°C or lower.

When the environment friendly gasoline base oil of the present invention is blended for the gasoline composition of the present invention, it may be desulfurized if necessary. The whole or a part of the fractions in the base oil my be desulfurized. The environment friendly gasoline base oil may be treated in a catalytic reforming unit so that the base oil may be blended as a gasoline base oil with a higher octane number in the gasoline of the present invention.

The content of the environment friendly gasoline

base oil of the present invention in the gasoline composition of the present invention is preferably 3 percent by volume or more, more preferably 5 percent by volume or more on the basis of the total mass of the gasoline with the objective of increasing the base oil originating from biomass. On the other hand, the base oil content is preferably 30 percent by volume or less, more preferably 25 percent by volume or less, 20 percent by volume or less in view of fuel consumption.

There is no particular restriction on base oils to be blended, other than the environment friendly gasoline base oil of the present invention. Therefore, any one or more types of gasoline base materials produced by any known process may be blended.

More specific examples of such base oils include straight propane fractions containing mainly propane and straight butane fractions containing mainly butane, produced in a distillation unit of crude oil, a naphtha reforming unit and an alkylation unit; straight desulfurized propane fractions and straight desulfurized butane fractions, produced by desulfurizing the foregoing fractions; cracked propane fractions containing mainly propane and propylene and cracked butane fractions containing mainly butane and butene, produced in a catalytic cracking unit; naphtha

fractions produced by atmospheric distillation of crude oil (whole-range naphtha); light fractions of naphtha; heavy fractions of naphtha; desulfurized whole-range naphtha produced by desulfurization of whole-range naphtha; desulfurized light naphtha produced by desulfurization of light naphtha; desulfurized heavy naphtha produced by desulfurization of heavy naphtha; isomerized gasolines produced by converting light naphthas to isoparaffin in an isomerization unit; alkylates produced by addition (alkylation) of lower olefins to hydrocarbons such as isobutane; reformed gasolines produced by a catalytic reforming process; raffinates which are residues produced by extracting aromatic components from reformed gasolines; light reformed gasolines that are light fractions of reformed gasolines; middle reformed gasolines that are middle fractions of reformed gasolines; heavy reformed gasolines that are heavy fractions of reformed gasolines; mixtures of two or more types of the foregoing reformed gasolines; catalytic cracked gasolines (whole-range cracked gasolines) produced by catalytic cracking; light cracked gasolines which are light fractions of catalytic cracked gasolines; heavy cracked gasolines which are heavy fractions of catalytic cracked

gasolines; hydrocracked gasolines produced by hydrocracking; polymerized gasolines produced by polymerizing olefin components; olefin fractions produced by dimerization of propylene or butene; paraffin fractions produced by hydrogenation of olefin fractions produced by dimerization of propylene or butene; de-n-paraffinizated oil; aromatic hydrocarbon compounds (toluene, aromatics having 8 carbon atoms (xylenes) and aromatics having 9 carbon atoms); and light fractions of GTL (Gas to Liquids) produced by F-T (Fischer-Tropsch) synthesis of natural gas after decomposed to carbon monoxide and hydrogen.

The blend amount of these base oils is optional as long as the gasoline of the present invention is adjusted to have its properties in the requisite ranges. Typical examples of the blend amount of the base oils are as follows:

(1) reformed gasoline: 0 to 80 percent by volume;

(2) cracked gasoline: 0 to 60 percent by volume;

(3) alkylate: 0 to 40 percent by volume;

(4) isomerized gasoline: 0 to 30 percent by volume.

The gasoline of the present invention may contain an oxygen-containing compound.

Examples of the oxygen-containing compound

include alcohols having 2 to 4 carbon atoms and ethers having 4 to 8 carbon atoms. Specific examples of the oxygen-containing compound include ethanol, methyl-tert-butyl-ether (MTBE), ethyl-tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and tert-amyl ethyl ether. Preferred are ethanol, MTBE, and ETBE. With the objective of inhibiting carbon dioxide emissions, ethanol originating from biomass and ETBE produced from ethanol originating from biomass are particularly preferably used. Since methanol may increase corrosivity and the aldehyde concentration in the exhaust gas, preferably it is not detected (0.5 percent by volume or less) when tested in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components".

The content of the oxygen-containing compound of the gasoline is preferably 3.8 percent by mass or less, more preferably 3.5 percent by mass or less, more preferably 2.7 percent by mass or less, and most preferably 1.3 percent by mass or less, in term of oxide, in view of compatibility to fuel system parts of an automobile and with the objective of preventing an increase in NOx in exhaust gas.

The research octane number (RON) of the gasoline of the present invention is necessarily 89.0 or greater,

preferably 90.0 or greater in view of anti-knocking properties, acceleration performance and drivability.

When the gasoline of the present invention is used for a regular gasoline-powered automobile, the RON is necessarily less than 96.0 because an increase in the CO_2 emissions upon production of the gasoline exceeds a reduction in the CO_2 emissions caused during automobile running. The motor octane number (MON) is preferably 80.0 or greater, more preferably 81.0 or greater with the objective of preventing the deterioration of anti-knocking properties at a higher speed running.

When the gasoline of the present invention is used for a premium gasoline-powered automobile, the RON is preferably 96.0 or greater, more preferably 98.0 or greater, more preferably 99.5 or greater, most preferably 100.0 or greater with the objective of maximizing the anti-knocking properties, acceleration performance and drivability of the premium gasoline-powered automobile. The MON is preferably 85.0 or greater, more preferably 87.0 or greater with the objective of preventing the deterioration of anti-knocking properties at a higher speed running.

The research octane number (RON) and motor octane number (MON) referred herein denote those measured in

accordance with JIS K 2280 "Petroleum products-Fuels-Determination of octane number, cetane number and calculation of cetane index".

The sulfur content of the gasoline of the present invention is necessarily 10 ppm by mass or less, preferably 8 ppm by mass or less, more preferably 5 ppm by mass or less. If the sulfur content is more than 10 ppm by mass, the gasoline adversely affects the performance of an exhaust gas purification catalyst, possibly leading to an increase in the concentrations of NOx, CO, and HC in the exhaust gas and an increase in the emissions of benzene.

The sulfur content referred herein denotes a value measured in accordance with JIS K 2541 "Crude oil and petroleum products-Determination of sulfur content".

The gasoline of the present invention is necessarily lead-free. The lead-free referred herein denotes that an alkyl lead compound such as tetraethyl lead is not added to gasoline and also means that the sulfur content is less or equal to the lower bounds (0.001 g/l) stipulated as acceptable in JIS K 2255 "Petroleum products-Gasoline-Determination of lead content" even though lead compounds are contained in an extremely trace amount.

The initial boiling point (IBP) of the gasoline

of the present invention is preferably 20°C or higher, more preferably 23°C or higher. If the IBP is lower than 20°C, the amount of hydrocarbons in the exhaust gas would be increased. The IBP is preferably 37°C or lower, more preferably 35°C or lower. If the IBP is higher than 37°C, low temperature drivability would be poor.

The 10% distillation temperature (T10) of the gasoline of the present invention is preferably 35°C or higher, more preferably 40°C or higher. If the T10 is lower than 35°C, the amount of hydrocarbons in the exhaust gas would be increased and high temperature drivability would be poor due to vapor lock. The T10 is preferably 70°C or lower, more preferably 60°C or lower. If the T10 is higher than 70°C, low temperature startability would be poor.

The 30% distillation temperature (T30) of the gasoline of the present invention is preferably 55°C or higher, more preferably 60°C or higher. If the T30 is lower than 55°C, fuel consumption would be poor. The T30 is preferably 77°C or lower, more preferably 75°C or lower, more preferably 70°C or lower. If the T30 is higher than 77°C, low and middle temperature drivability would be poor.

The 50% distillation temperature (T50) of the

gasoline of the present invention is preferably 75°C or higher, more preferably 80°C or higher with the objective of preventing the deterioration of fuel consumption. The T50 is preferably 110°C or lower, more preferably 105°C or lower, more preferably 100°C or lower with the objective of preventing the deterioration of normal temperature drivability.

The 70% distillation temperature (T70) of the gasoline of the present invention is preferably 95°C or higher. If the T70 is lower than 95°C, fuel consumption would be poor. The T70 is preferably 135°C or lower, more preferably 130°C or lower. If the T70 is higher than 135°C, low and middle temperature drivability of a cold engine would be poor and the amounts of hydrocarbons in the exhaust gas and deposit on intake valves or in a combustion chamber would be increased.

The 90% distillation temperature (T90) of the gasoline of the present invention is preferably 115°C or higher, more preferably 120°C or higher. If the T90 is lower than 115°C, fuel consumption would be poor. The T90 is preferably 180°C or lower, more preferably 175°C or lower, more preferably 170°C or lower, more preferably 165°C or lower with the objective of preventing the deterioration of low and normal

temperature drivability of a cold engine, the dilution of an engine oil with the gasoline, an increase in hydrocarbon exhaust gas, the degradation of an engine oil, and sludge formation.

The end point of the gasoline of the present invention is preferably 150°C or higher. The end point is also preferably 220°C or lower, more preferably 215°C or lower, more preferably 200°C or lower, more preferably 195°C or lower. If the end point is higher than 220°C, deposits on an intake valve or in a combustion chamber tends to be increased and also smoldering of a spark plug may occur.

The IBP, T10, T30, T50, T70, T90, and EP referred herein denote the values (°C) measured in accordance with JIS K 2254 "Petroleum products-Determination of distillation characteristics".

The reid vapor pressure (RVP) of the gasoline of the present invention is preferably adjusted depending on the season or district where the gasoline is used. More specifically, for warm season and district use, the RVP is preferably from 44 to 72 kPa, more preferably from 44 to 65 kPa, more preferably from 50 to 65 kPa, most preferably from 55 to 65 kPa. For cold season and district use, the RVP is preferably from 60 to 93 kPa, more preferably from 65 to 93 kPa, more preferably from

70 to 93 kPa, most preferably from 70 to 88 kPa. A too high RVP may cause some defects in drivability due to vapor lock. A too low RVP may cause the deterioration of startability of a cold engine. The vapor pressure (RVP) referred herein denotes the value (kPa) measured in accordance with JIS K 2258 "Testing Method for Vapor Pressure of Crude Oil and Petroleum Products (Reid Method)".

When the gasoline of the present invention is used in a regular gasoline-powered automobile, the density at 15°C of the gasoline is preferably 0.690 g/cm^3 or greater, more preferably 0.700 g/ cm^3 or greater, more preferably 0.710 g/ cm^3 or greater, most preferably 0.715 g/ cm^3 or greater with the objective of preventing the deterioration of fuel consumption and also preferably 0.783 g/cm^3 or less, more preferably 0.760 g/ cm^3 or less, more preferably 0.750 g/ cm^3 or less, most preferably 0.745 g/ cm^3 or less with the objective of preventing the deterioration of acceleration performance or smoldering of a plug.

When the gasoline of the present invention is used in a premium gasoline-powered automobile, the density at 15°C of the gasoline is preferably 0.700 g/ cm^3 or greater, more preferably 0.710 g/ cm^3 or greater, more preferably 0.720 g/ cm^3 or greater, most preferably

0.730 g/ cm^3 or greater and is preferably 0.783 g/ cm^3 or lower, more preferably 0.770 g/ cm^3 or lower, more preferably 0.760 g/ cm^3 or lower with the objective of preventing the deterioration of acceleration performance or smoldering of a plug.

The density at 15°C referred herein denotes the value (g/cm^3) measured in accordance with JIS K 2249 "Crude petroleum and petroleum products-Determination of density and petroleum measurement tables based on a reference temperature (15°C)".

The oxidation stability of the gasoline of the present invention is preferably 240 minutes or longer, more preferably 480 minutes or longer, more preferably 1440 minutes or longer with the objective of preventing gum formation during storage.

The oxidation stability referred herein denotes the value (minute) measured in accordance with JIS K 2287 "Testing Method for Oxidation Stability of Gasoline (Induction Period Method)".

The corrosiveness to copper (50°C, 3 hours) of the gasoline of the present invention is preferably 1 or less, more preferably 1a. If the corrosiveness to copper is greater than 1, the conduits of a fuel system may be corroded.

The corrosiveness to copper referred herein

denotes the value measured in accordance with JIS K 2513 "Petroleum products-Corrosiveness to copper-Copper strip test" (Test temperature: 50°C, Test time: 3 hours).

The washed existent gum content of the gasoline of the present invention is preferably 5 mg/100 ml or less, more preferably 3 mg/100 ml or less, more preferably 1 mg/100 ml or less. The unwashed existent gum content of the gasoline is preferably 20 mg/100 ml or less, more preferably 10 mg/100 ml or less, more preferably 5 mg/100 ml or less. If the washed and unwashed existent gum contents exceed the above values, deposit may formed in a fuel introducing system or intake valves may agglutinate.

The washed and unwashed existent gum contents referred herein denote the values (mg/100 ml) measured in accordance with JIS K 2261 "Petroleum Products-Motor gasoline and aviation fuels-Determination of existent gum-Jet evaporation method".

The benzene content of the gasoline of the present invention is preferably 1 percent by volume or less, more preferably 0.5 percent by volume of less. If the benzene content is more than 1 percent by volume, the benzene concentration in the exhaust gas may be increased.

The benzene content referred herein denotes the benzene content (percent by volume) measured in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components-Determination of aromatic by gas chromatography".

When the gasoline of the present invention is used in a regular gasoline-powered automobile, the aromatic content of the gasoline is preferably 40 percent by volume or less, more preferably 35 percent by volume or less, more preferably 30 percent by volume or less. If the aromatic content is more than 40 percent by volume, deposits on an intake valve or in a combustion chamber tends to be increased and also smoldering of a spark plug may occur. Further, the benzene concentration in the exhaust gas may be increased. The aromatic content is preferably 10 percent by volume or more, more preferably 15 percent by volume or more. If the aromatic content is lower than 10 percent by volume, fuel consumption would be poor.

When the gasoline of the present invention is used in a premium gasoline-powered automobile, the aromatic content of the gasoline is preferably 45 percent by volume or less, more preferably 42 percent by volume or less, more preferably 40 percent by volume of less. If the aromatic content is more than 45 percent by volume

or more, deposits on an intake valve or in a combustion chamber tends to be increased and also smoldering of a spark plug may occur. Further, the benzene concentration in the exhaust gas may be increased. The aromatic content is preferably 20 percent by volume or more, preferably 25 percent by volume or more. If the aromatic content is lower than 20 percent by volume, fuel consumption would be poor.

The aromatic content referred herein denotes the aromatic content (percent by volume) in a gasoline measured in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components-Fluorescent indicator adsorption method".

The olefin content of the gasoline of the present invention is preferably 35 percent by volume or less, more preferably 25 percent by volume or less. If the olefin content is more than 35 percent by volume, the resulting gasoline would be poor in oxidation stability and increase deposits on an intake valve.

The olefin content referred herein denotes the olefin content (percent by volume) in a gasoline measured in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components-Fluorescent indicator adsorption method".

The amount of entrained kerosene in the gasoline

of the present invention is preferably 4 percent by volume or less. If the entrained amount exceeds 4 percent by volume, engine startability would be poor.

The amount of entrained kerosene referred herein is determined by the content of n-paraffinic hydrocarbons having 13 and 14 carbon atoms on the basis of the total mass of a gasoline and denotes that the corresponding value of kerosene obtained in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components" is 4 percent by volume or less.

The manganese content of the gasoline is preferably 2 ppm by mass or less, more preferably 1 ppm by mass. The iron content of the gasoline is preferably 2 ppm by mass or less, more preferably 1 ppm by mass or less. The sodium content of the gasoline is preferably 2 ppm by mass or less, more preferably 1 ppm by mass or less. The potassium content of the gasoline is preferably 2 ppm by mass or less, more preferably 1 ppm by mass or less. The phosphorus content of the gasoline is preferably 2 ppm by mass or less, preferably 1 ppm by mass or less, more preferably 0.2 ppm by mass or less. If the contents of manganese, iron, sodium, potassium, and phosphorus exceed the above-described values, the efficiency of an exhaust gas purifying system may be degraded due to an increase in deposition

of these substances on an exhaust gas purifying catalyst, degradation of a catalyst support, and deterioration of an air-fuel ratio sensor.

The manganese, iron, and sodium contents referred herein denote the values measured by "combustion ashing- inductively coupled plasma atomic emission spectrometry". The potassium content referred herein denotes the value measured by "combustion ashing-atomic absorption spectrometry". The phosphorus content referred herein denotes the value measured in accordance with ASTM D3231 "Standard Test Method for Phosphorus in Gasoline".

The procedures of "combustion ashing-inductively coupled plasma atomic emission spectrometry" and "combustion ashing-atomic absorption spectrometry" are as follows:

(1) 20g of a sample is weighed into a platinum dish;

(2) 0.4 g of powdery sulfur is added so as to prevent sublimation of the constituent elements and the dish is placed on a sand bath at a temperature of 150°C for one hour so as to remove the volatile matters;

(3) the residue is combusted;

(4) the combusted residue is ashed in an electric furnace kept at a temperature of 500°C for 2 to 3 hours;

(5) the ash is dissolved with 2 to 3 ml of concentrated sulfuric acid and diluted to be 20 mL in volume;

(6) the manganese, iron, and sodium contents are analyzed using an inductively coupled plasma atomic emission spectrometry analyzer (ICPS-8000 manufactured by SHIMADZU CORPORATION), and the phosphorus content is analyzed using an atomic absorption photometer (Z6100 manufactured by Hitachi, Ltd.).

The gasoline of the present invention preferably contains an anti-oxidant and a metal deactivator for storage stability. Specific examples of the anti-oxidant include phenylene diamine-based anti-oxidants such as N,N'-diisopropyl-p-phenylene diamine and N,N'-diisobutyl-p-phenylene diamine and alkyl phenol-based anti-oxidants such as hindered phenols typically 2,6-di-t-butyl-4-methyl phenol. Examples of the metal deactivator include compounds known as metal deactivators, i.e., amine carbonyl condensation compounds such as N,N'-disalicylidene-1,2-diamino propane.

There is no particular restriction on the amount of the anti-oxidant or metal deactivator to be added.

The anti-oxidant or metal deactivator is added so that the above-described oxidation stability of the gasoline falls within the preferable range and the unwashed existent gum content of the gasoline after other additives are added thereto falls within the above-described preferable range. More specifically, the anti-oxidant is added in an amount of preferably 5 to 100 mg/l, more preferably 10 to 50 mg/l. The metal deactivator is added in an amount of preferably 0.5 to 10 mg/l, more preferably 1 to 5 mg/l.

The gasoline of the present invention may contain a detergent-dispersant so as to prevent the accumulation of deposits on an intake valve or the like. The detergent-dispersant may be any compound known as a detergent-dispersant for gasoline such as succinimide, polyalkyl amine, and polyether amine. Among these, preferred are those which can be decomposed completely when subjected to thermal decomposition at a temperature of 300°C . The detergent-dispersant is more preferably polyisobutenyl amine and/or polyether amine.

The content of the detergent-dispersant is preferably from 25 to 1000 mg per liter of the gasoline. With the objective of preventing the formation of deposits on an intake valve and reducing deposits in

a combustion chamber, the content is more preferably from 50 to 500 mg, most preferably from 100 to 300 mg. The effective components contributive to detergency of some detergent-dispersants are diluted with a suitable solvent. In the case of using such detergent-dispersants, the above-described content means the content of the effective components.

The gasoline of the present invention may contain a friction modifier so as to improve its lubricity. When the gasoline is used in a premium gasoline-powered automobile in particular, the gasoline preferably contains a friction modifier.

Examples of the friction modifier include alcohols; alcohol compounds of 1 to 30 carbon atoms, having 1 to 4 hydroxyl groups; carboxylic acids; hydroxyl group-containing esters which are reaction products of monocarboxylic acids and glycol or trihydric alcohols; esters of polycarboxylic acids and polyhydric alcohols; esters of polyhydric alcohols and nitrogen compounds having a chemical composition containing >NR (R is a hydrocarbon group having 5 to 40 carbon atoms and having one or more substituents; and amide compounds of carboxylic acids and alcohol amines. These friction modifiers may be used alone or in combination. Preferred are hydroxyl

group-containing esters which are reaction products of monocarboxylic acids having 10 to 25 carbon atoms and glycol or trihydric alcohols and/or amide compounds of carboxylic acids having 5 to 25 carbon atoms and alcohol amines. More preferred are esters of monocarboxylic acids having 10 to 25 carbon atoms and glycerin esters and/or amide compounds of monocarboxylic acids having 5 to 25 carbon atoms and diethanol amine.

There is no particular restriction on the amount of the friction modifier. However, the friction modifier is preferably added so that the unwashed existent gum content of the gasoline after other additives are added thereto falls within the above-described preferable range. The friction modifier is added in an amount of preferably 10 to 300 mg, more preferably 30 to 250 mg per liter of the gasoline with the objective of improving fuel consumption and an engine output and because a further improvement may not be expected when it is added more.

Some products in the name of friction modifier are commercially available in a state wherein the effective components contributing to wear resistance is diluted with a suitable solvent. In the case where such products are added to the gasoline of the present invention, the above-described amount means the amount

of the effective components.

Examples of other additives which may be added to the gasoline of the present invention include surface ignition inhibitors such as organic phosphorus compounds, anti-icing agents such as polyhydric alcohols and ethers thereof, combustion improvers such as alkali or alkaline metal salts of organic acids and sulfuric esters of higher alcohols, anti-static additives such as anionic, cationic, and amphoteric surface active agents, coloring agents such as azo dye, rust inhibitors such as organic carboxylic acids , their derivatives and alkenyl succinic acid esters, water draining agents such as sorbitan esters, markers such as quinizarin and coumarin, and odorants such as perfumes synthesized from natural essential oils.

These additives may be added alone or in combination, and the total amount is preferably 0.1 percent by mass or less on the basis of the total mass of the gasoline.

The gasoline fraction produced by the hydrotreatment process of the present invention may also be used as a feedstock for the use in a catalytic reforming unit. When the feedstock contains biomass, it can advantageously provide an effect to reduce

carbon dioxide emissions estimated in view of life cycle (LCA-CO_2) upon production of hydrogen, fuel for gasoline engines and benzene, toluene and xylene, which are basic raw materials of petroleum chemical products. That is, the present invention can provide hydrogen, fuel for gasoline engines and basic raw materials of petroleum chemical products such as benzene, toluene and xylene, all of which can reduce LCA-CO_2 sufficiently.

The fractions of the hydrotreated oil produced by the present invention may be partially reformed in a steam reforming unit or a catalytic reforming unit thereby producing hydrogen. When the feedstock contains biomass, the resulting hydrogen has properties, so-called carbon neutral and thus can reduce environment loads upon production of hydrogen and/or gasoline base oil.

With regard to the hydrotreated oil produced by the present invention, a kerosene fraction with a boiling point of 220 to 350°C can be suitably used as diesel gas oil or heavy base oil. When this fraction is used as diesel gas oil, its sulfur content is preferably 10 ppm by mass or less. If the sulfur content exceeds the upper limit, the fraction would adversely affect a filter or catalyst used in the

exhaust gas processing device of a diesel engine. The hydrotreated oil may be used alone as diesel gas oil or heavy base oil but may be used as diesel gas oil or heavy base oil, mixed with components such as other base oils. Examples of the other base oils include gas oil fractions and/or kerosene fractions that are produced in a conventional hydrorefining process and residue fractions produced by the present invention. Further, the kerosene fraction may be mixed with a synthetic gas oil or kerosene produced through a Fischer-Tropsch reaction using synthetic gas as the feedstock. The synthetic gas oil or kerosene contains little aromatic and contains saturated hydrocarbons as the main component and is high in cetane number. There is no particular restriction on the method of producing the synthetic gas. Therefore, any conventional method may be used.

[Applicability in the Industry]

The present invention provides a process of hydrotreating a feedstock comprising a fat component originating from an animal or vegetable oil. The present invention also provides an environment friendly gasoline base oil and an unleaded gasoline composition, which are effectively accomplish a

reduction in carbon dioxide emissions, through the hydrotreatment process.

[Examples]

Hereinafter, the present invention will be described in more details by way of the following examples and comparative examples, which should not be construed as limiting the scope of the invention.

(Preparation of catalyst A)

A Y-type zeolite with a ratio of the silica to the alumina (SiO_2/Al_2O_3) of 5 was ultra-stabilized by hydrothermal treatment at 780°C for one hour under saturated steam atmosphere using a steaming device and then subjected to acid treatment with a 1N nitric acid aqueous solution thereby producing 210 g of a proton-type ultra-stabilized Y-type zeolite with a lattice constant of 24.33 Å, determined by X-ray diffraction and a ratio of the silica to the alumina (SiO_2/Al_2O_3) of 30.

On the other hand, 185 g of sodium silicate No. 3 was added to 3000 g of an aqueous solution of 5 percent by mass of sodium aluminate and then put into a vessel kept at a temperature of 65°C. In a separate vessel kept at a temperature of 65°C, 3000 g of an aqueous solution of 2.5 percent by mass of aluminum sulfate were

prepared. The foregoing sodium aluminate aqueous solution was added dropwise thereto. When the pH of the mixture reached 7.0, the addition was stopped. The resulting slurry product was passed through a filter thereby producing a cake-like slurry.

The resulting slurry was transferred to a vessel equipped with a reflux condenser, and 150 ml of distilled water and 10 g of an aqueous solution of 27% ammonia were added thereto, followed by 20 hour stirring at 75°C. The slurry was put into a kneader and kneaded, while being heated at a temperature of 80°C or higher to remove water, thereby producing a clay-like kneaded mass. To the kneaded mass were added 186 g of the foregoing ultra-stabilized Y-type zeolite, followed by further kneading. The resulting kneaded mass was extruded into the form of a cylinder with a diameter of 1.5 mm, through an extruder and then dried at a temperature of 110°C for one hour and calcined at a temperature of 550°C thereby producing molded support A.

Into an eggplant type flak were put 50 g of the resulting molded support A and 35 ml of a mixed aqueous solution of tetramine platinum (II) chloride and tetamine palladium (II) chloride. Whereby, the metals contained in the solution was impregnated into the

support while being deaerated with a rotary evaporator and dried at a temperature of 110°C and then calcined at a temperature of 350°C thereby producing catalyst A. The amounts of platinum and palladium supported on the catalyst were 0.5 percent by mass and 0.7 percent by mass, respectively, on the basis of the total mass of the catalyst.

(Preparation of catalyst B)

Into a vessel kept at a temperature of 65°C were put 3000 g of an aqueous solution of 5 percent by mass of sodium aluminate. In a separate vessel kept at a temperature of 65°C were prepared 3000 g of an aqueous solution of 2.5 percent by mass of aluminum sulfate, followed by dropwise addition of the sodium aluminate aqueous solution. The addition was stopped when the pH of the mixture reached 7.0, and the resulting slurry product was passed through a filter thereby producing a cake-like slurry.

The resulting slurry was transferred to a vessel equipped with a reflux condenser, and 150 ml of distilled water and 10 g of an aqueous solution of 27% ammonia were added thereto, followed by 20 hour stirring at 75°C. The slurry was put into a kneader and kneaded, while being heated at a temperature of 80°C or higher to remove water, thereby producing a

clay-like kneaded mass. The resulting kneaded mass was extruded into the form of a cylinder with a diameter of 1.5 mm, through an extruder and then dried at a temperature of 110°C for one hour and calcined at a temperature of 550°C thereby producing molded support B.

Into an eggplant type flak were put 50 g of the resulting molded support B and 35 ml of a mixed aqueous solution of dinitroamine platinum (II) and dinitroamine palladium (II). The metals contained in the solution was impregnated into the support while being deaerated with a rotary evaporator and dried at a temperature of 110°C and then calcined at a temperature of 350°C thereby producing catalyst B. The amounts of platinum and palladium supported on the catalyst were 0.5 percent by mass and 0.7 percent by mass, respectively, on the basis of the total mass of the catalyst.

(Preparation of catalyst C)

Into an eggplant type flak were put 50 g of molded support A produced above and then a solution containing 10.0 g of molybdenum trioxide, 18.3 g of nickel (II) nitrate hexahydrate, 0.9 g of phosphoric acid (85 percent concentration) and 4.0 g of malic acid. The metals contained in the solution was impregnated into

the support while being deaerating with a rotary evaporator and dried at a temperature of 120°C for one hour and calcined at a temperature of 550°C, thereby producing catalyst C. The amounts of nickel and molybdenum supported on catalyst C were 4.0 percent by mass (in the form of nickel oxide) and 16.0 percent by mass (in the form of molybdenum oxide), respectively, in terms of oxide, on the basis of the total mass of the catalyst.

(Preparation of catalyst D)

Into an eggplant type flak were put 50 g of molded support B produced above and a solution containing 10.0 g of molybdenum trioxide, 18.3 g of nickel (II) nitrate hexahydrate, 0.9 g of phosphoric acid (85 percent concentration) and 4.0 g of malic acid. The metals contained in the solution was impregnated into the support while being deaerating with a rotary evaporator and dried at a temperature of 120°C for one hour and calcined at a temperature of 550°C, thereby producing catalyst D. The amounts of nickel and molybdenum supported on catalyst D were 4.0 percent by mass (in the form of nickel oxide) and 16.0 percent by mass (in the form of molybdenum oxide), respectively, in terms of oxide, on the basis of the total mass of the catalyst.

(Example 1)

Catalyst A (50 ml) was charged into each of a first reaction tube (inner diameter of 20mm) and a second reaction tube (inner diameter of 20mm), both of which were installed in series in a fixed bed circulation type reactor. Thereafter, the catalyst was subjected to a reduction treatment under conditions where the average catalyst layer temperature was 300°C, the hydrogen partial pressure was 5 MPa, the hydrogen gas rate was 83 ml/min, for 6 hours.

Thereafter, a feedstock that was palm oil (the ratio of the compound having a triglyceride structure in the oxygen-containing compound: 98 percent by mole) was hydrotreated using the catalyst. The feedstock had a density at 15°C of 0.916 g/ml and an oxygen content of 11.4 percent by mass. The hydrotreatment was carried out under conditions where the reaction temperature, pressure and liquid hourly space velocity in the first and second reaction tubes were 415°C, 5 MPa and 0.45 h^{-1}, respectively. The volume ratio of hydrogen gas introduced between the first and second reaction tubes (quenching hydrogen ratio) was 20 percent by volume of the total hydrogen introduced in the reactor, and the hydrogen/oil ratio determined by the total hydrogen introduced in the reactor was 1010

NL/L. The resulting hydrotreated oil was measured to determine the oxygen and sulfur contents, the yield of each fraction, and the oxygen and normal paraffin contents in the naphtha fraction with a boiling point range of 80 to 135°C (fraction corresponding to hydrocarbons having 5 to 10 carbon atoms). The results are set forth in Table 1 below.

(Comparative Example 1)

Hydrotreatment was carried out with the same procedures of Example 1 except for using catalyst B instead of catalyst A. The resulting hydrotreated oil was measured in the same respects as in Example 1. The results are set forth in Table 1.

(Example 2)

Catalyst C (50 ml) was charged into each of a first reaction tube (inner diameter of 20mm) and a second reaction tube (inner diameter of 20mm), both of which were installed in series in a fixed bed circulation type reactor. Thereafter, the catalyst was pre-sulfided with a straight gas oil (sulfur content: 3 percent by mass) to which dimethyldisulfide had been added, under conditions where the average catalyst layer temperature was 300°C, the hydrogen partial pressure

was 6 MPa, the liquid hourly space veloxity was 1 h^{-1}, and the hydrogen/oil ratio was 200 NL/L, for 4 hours.

Thereafter, a feedstock prepared by adding dimethylsulfide to palm oil (the ratio of the compound having a triglyceride structure in the oxygen-containing compound: 98 percent by mole) so that the sulfur content of the feedstock was adjusted to 51 ppm by mass was subjected to hydrotreatment using the catalyst. The feedstock had a density at 15°C of 0.916 g/ml and an oxygen content of 11.4 percent by mass. The hydrotreatment was carried out under conditions where the reaction temperature, pressure and liquid hourly space velocity in the first and second reaction tubes were 425°C, 5 MPa and 0.4 h^{-1}, respectively. The volume ratio of hydrogen gas introduced between the first and second reaction tubes (quenching hydrogen ratio) was 20 percent by volume of the total hydrogen introduced in the reactor, and the hydrogen/oil ratio determined by the total hydrogen introduced in the reactor was 1010 NL/L. The resulting hydrotreated oil was measured to determine the oxygen and sulfur contents, the yield of each fraction, and the oxygen, sulfur and normal paraffin contents in the naphtha fraction with a boiling point range of 80 to 135°C (fraction corresponding to hydrocarbons having 5 to 10 carbon

atoms). The results are set forth in Table 2 below.

(Comparative Example 2)

Hydrotreatment was carried out with the same procedures of Example 2 except that catalyst D was used instead of catalyst C and the reaction temperature in the first and second reaction tubes was changed to 430°C. The resulting hydrotreated oil was measured in the same respects as in Example 2. The results are set forth in Table 1.

(Examples 3 to 6, and Comparative Examples 3 and 4)

Catalyst E was prepared by supporting 0.5 percent by mass of platinum and 0.7 percent by mass of palladium that belong to the Group 8 of the periodic table, on a support composed of 55 percent by mass of an ultra-stable Y-type zeolite containing a metallosilicate with a faujasite type structure, 15.75 percent by mass of silica, and 29.25 percent by mass of alumina. The silica/alumina ratio of the ultra-stable Y-type zeolite was 33.

The feedstock to be hydrotreated was palm oil that was biomass vegetable oil. The palm oil had a triglyceride content of 98 percent by mole, an oxygen content of 11.4 percent by mass, and a sulfur content

of less than 0.1 ppm by mass.

After catalyst E was subjected to a pre-reduction treatment, hydrotreatment was carried out by contacting the catalyst with the feedstock that was palm oil, under conditions where the reaction temperature was 425°C, the hydrogen pressure was 5 MPa, the liquid hourly space velocity was 0.4 h^{-1}, and the hydrogen/oil ratio was 1010 NL/L. The resulting oil was distilled thereby producing biomass hydrotreated base oil E that is a fraction having a distillation temperature range of 35 to 135°C. The resulting biomass base oil E had a oxygen content of less than 0.1 percent by mass, a sulfur content of less than 0.1 ppm by mass, and a normal paraffin content of 24.8 percent by mass.

The gasoline composition of Example 3 was prepared by blending 10 percent by volume of biomass hydrotreated base oil E, gasoline base oils such as a light reformed gasoline (distillation temperature range of 27 to 128°C, density of 0.690 g/cm^3, aromatic content of 23 percent by volume), a middle-heavy reformed gasoline (distillation temperature range of 92 to 195°C, density of 0.853 g/cm^3, aromatic content of 90 percent by volume), a light catalytic cracked gasoline (distillation temperature range of 27 to 81°C,

density of 0.656 g/cm^3, olefin content of 47 percent by volume), a heavy catalytic cracked gasoline (distillation temperature range of 75 to 198°C, density of 0.764 g/cm^3, olefin content of 33 percent by volume), an alkylate (distillation temperature range of 33 to 179°C, density of 0.696 g/cm^3, saturate content of 100 percent by volume), a light naphtha(distillation temperature range of 28 to 105°C, density of 0.637 g/cm^3, and saturate content of 99 percent by volume), toluene, and normal butane, an anti-oxidant, and a metal deactivator.

The gasoline composition of Example 4 was prepared by blending 12 percent by volume of biomass hydrotreated base oil E, 7 percent by volume of BTBE produced from a biomass-originating ethanol, gasoline base oils such as a light reformed gasoline (distillation temperature range of 27 to 128°C, density of 0.690 g/cm^3, aromatic content of 23 percent by volume), a middle-heavy reformed gasoline (distillation temperature range of 92 to 125°C, density of 0.853 g/cm^3, aromatic content of 90 percent by volume), a light catalytic cracked gasoline (distillation temperature range of 27 to 81°C, density of 0.656 g/cm^3, olefin content of 47 percent by volume), a heavy catalytic cracked gasoline (distillation

temperature range of 75 to 198°C, density of 0.764 g/cm^3, olefin content of 33 percent by volume), an alkylate (distillation temperature range of 33 to 179°C, density of 0.696 g/cm^3, saturate content of 100 percent by volume), a light naphtha(distillation temperature range of 28 to 105°C, density of 0.637 g/cm^3, and saturate content of 99 percent by volume), toluene, and normal butane, an anti-oxidant, and a metal deactivator.

Catalyst F was prepared by supporting 4.0 percent by mass of nickel (in the form of nickel oxide) and 16.0 percent by mass of molybdenum (in the form of molybdenum trioxide) that belong to the Groups 8 and 6A of the periodic table, respectively on a support composed of 55 percent by mass of an ultra-stable Y-type zeolite containing a crystalline metallosilicate with a faujasite type structure, 15.75 percent by mass of silica, and 29.25 percent by mass of alumina. The silica/alumina ratio of the ultra-stable Y-type zeolite was 30.

The feedstock to be hydrotreated was prepared by adding dimethyldisulfide to palm oil that was biomass vegetable oil (triglyceride content of 98 percent by mole, oxygen content of 11.4 percent by mass, and sulfur content of less than 0.1 ppm by mass) so that the sulfur

content of the feedstock was adjusted to 51 ppm by mass.

Thereafter, hydrotreatment was carried out by contacting the catalyst with the feedstock, i.e., the forgoing dimethyldisulfide-added palm oil, under conditions where the reaction temperature was 425°C, the hydrogen pressure was 5 MPa, the liquid hourly space velocity was 0.4 h^{-1}, and the hydrogen/oil ratio was 1010 NL/L. The resulting oil was distilled thereby producing biomass hydrotreated base oil F that is a fraction having a distillation temperature range of 35 to 135°C. The resulting biomass base oil F had a oxygen content of less than 0.1 percent by mass, a sulfur content of 1.3 ppm by mass, and a normal paraffin content of 24.3 percent by mass.

The gasoline composition of Example 5 was prepared by blending 10 percent by volume of biomass hydrotreated base oil F, gasoline base oils such as a light reformed gasoline (distillation temperature range of 27 to 128°C, density of 0.690 g/cm^3, aromatic content of 23 percent by volume), a middle-heavy reformed gasoline (distillation temperature range of 92 to 195°C, density of 0.853 g/cm^3, aromatic content of 90 percent by volume), a light catalytic cracked gasoline (distillation temperature range of 27 to 81°C, density of 0.656 g/cm^3, olefin content of 47 percent

by volume), a heavy catalytic cracked gasoline (distillation temperature range of 75 to 198°C, density of 0.764 g/cm^3, olefin content of 33 percent by volume), an alkylate (distillation temperature range of 33 to 179°C, density of 0.696 g/cm^3, saturate content of 100 percent by volume), a light naphtha(distillation temperature range of 28 to 105°C, density of 0.637 g/cm^3, and saturate content of 99 percent by volume), toluene, and normal butane, an anti-oxidant, a metal deactivator, and a detergent-dispersant.

The gasoline composition of Example 6 was prepared by blending 10 percent by volume of biomass hydrotreated base oil F, 3 percent by volume of a biomass-originating ethanol, gasoline base oils such as a light reformed gasoline (distillation temperature range of 27 to 128°C, density of 0.690 g/cm^3, aromatic content of 23 percent by volume), a middle-heavy reformed gasoline (distillation temperature range of 92 to 195°C, density of 0.853 g/cm^3, aromatic content of 90 percent by volume), a light catalytic cracked gasoline (distillation temperature range of 27 to 81°C, density of 0.656 g/cm^3, olefin content of 47 percent by volume), a heavy catalytic cracked gasoline (distillation temperature range of 75 to 198°C, density of 0.764 g/cm^3, olefin content of 33 percent by volume),

an alkylate (distillation temperature range of 33 to 179°C, density of 0.696 g/cm^3, saturate content of 100 percent by volume), a light naphtha(distillation temperature range of 28 to 105°C, density of 0.637 g/cm^3, and saturate content of 99 percent by volume), toluene, and normal butane, an anti-oxidant, a metal deactivator, a detergent-dispersant, and a friction modifier.

The gasoline composition of Comparative Example 3 was prepared by blending 55 percent by volume of biomass hydrotreated base oil E, gasoline base oils such as a light reformed gasoline (distillation temperature range of 27 to 128°C, density of 0.690 g/cm^3, aromatic content of 23 percent by volume), a middle-heavy reformed gasoline (distillation temperature range of 92 to 195°C, density of 0.853 g/cm^3, aromatic content of 90 percent by volume), a light catalytic cracked gasoline (distillation temperature range of 27 to 81°C, density of 0.656 g/cm^3, olefin content of 47 percent by volume), a heavy catalytic cracked gasoline (distillation temperature range of 75 to 198°C, density of 0.764 g/cm^3, olefin content of 33 percent by volume), an alkylate (distillation temperature range of 33 to 179°C, density of 0.696 g/cm^3, saturate content of 100 percent by volume), a light naphtha(distillation temperature range of 28 to 105°C,

density of 0.637 g/cm^3, and saturate content of 99 percent by volume), toluene, and normal butane, an anti-oxidant, and a metal deactivator.

The composition of Comparative Example 4 is a commercially available regular gasoline.

Table 3 sets forth the properties of each gasoline composition.

(Examples 7 to 10, and Comparative Examples 5 and 6)

The gasoline composition of Example 7 was prepared with the same procedures of Example 3 except that the amount of biomass hydrotreated base oil E was changed to 5 percent by volume.

The gasoline composition of Example 8 was prepared with the same procedures of Example 4 except that the amount of biomass hydrotreated base oil E was changed to 5 percent by volume.

The gasoline composition of Example 9 was prepared with the same procedures of Example 5 except that the amount of biomass hydrotreated base oil F was changed to 5 percent by volume.

The gasoline composition of Example 10 was prepared with the same procedures of Example 6 except that the amount of biomass hydrotreated base oil F was changed to 7 percent by volume.

The gasoline composition of Comparative Example 5 was prepared with the same procedures of Comparative Example 3 except that the amount of biomass hydrotreated base oil E was changed to 40 percent by volume.

The composition of Comparative Example 6 is a commercially available premium gasoline.

Table 5 sets forth the properties of each gasoline composition.

(Determination of properties)

The properties of the gasoline compositions of the examples and comparative examples were determined by the following methods.

Research octane number and motor octane numbers are values measured in accordance with JIS K 2280 "Petroleum products-Fuels-Determination of octane number, cetane number and calculation of cetane index".

Sulfur content was measured in accordance with JIS K 2541 "Crude oil and petroleum products-Determination of sulfur content".

Lead content was measured in accordance with JIS K 2255 "Petroleum products-Gasoline-Determination of lead content".

Distillation characteristics (IBP, T10, T30, T50,

T70, T90, and EP) are all measured in accordance with JIS K 2254 "Petroleum products-Determination of distillation characteristics".

Vapor pressure (@37.8°C) was measured in accordance with JIS K 2258 "Testing Method for Vapor Pressure of Crude Oil and Petroleum Products (Reid Method)".

Density (@15°C) was measured in accordance with JIS K 2249 "Crude petroleum and petroleum products-Determination of density and petroleum measurement tables based on a reference temperature (15°C)".

Oxidation stability was measured in accordance with JIS K 2287 "Testing Method for Oxidation Stability of Gasoline (Induction Period Method)".

Corrosiveness to copper was measured in accordance with JIS K 2513 "Petroleum products-Corrosiveness to copper-Copper strip test" (Test temperature: 50°C, Test time: 3 hours).

Unwashed existent gum and washed existent gum contents were measured in accordance with JIS K 2261 "Petroleum Products-Motor gasoline and aviation fuels-Determination of existent gum-Jet evaporation method".

Benzene content was measured in accordance with

JIS K 2536 "Liquid petroleum products-Testing method of components-Determination of aromatic components by gas chromatography".

Aromatic and olefin contents were measured in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components-Fluorescent indicator adsorption method".

Kerosene content was measured in accordance with "Liquid petroleum products-Testing method of components".

Manganese, iron and sodium contents were measured by "combustion ashing-inductively coupled plasma atomic emission spectrometry". Potassium content was measured by "combustion ashing-atomic absorption spectrometry". Phosphorus content was measured in accordance with ASTM D3231 "Standard Test Method for Phosphorus in Gasoline".

(Content of biomass-originating base oil)

For the compositions of the examples and comparative examples, the content of the biomass-originating base oils and the content of the vegetable oil-originating base oils of the biomasses were indicated from the blend ratio of the base oils.

(Acceleration performance evaluation)

On a chassis dynamometer whose environment

temperature and humidity were kept at 25°C and 50%, acceleration performance was evaluated using the following test vehicles (vehicle 1 for regular gasolines and vehicle 2 for premium gasolines). After the vehicles was sufficiently warmed up, full throttle acceleration from 50 km/h to 110 km/h in D-range (OD was on) was repeated 10 times so as to measure the time required until the speed reached from 60 km/h to 100 km/h. The average time of the 7 acceleration runs excluding the first 3 time run was defined as acceleration time.

[Test Vehicle]: vehicle 1

Engine: in-line four-cylinder (regular gasoline-powered)

Displacement: 1498 cc

Injection mode: multi point injection

Transmission: automatic transmission

Exhaust-gas purifying system: ternary catalyst, air/fuel feedback control system Adopted to 2000 Exhaust Gas Emission Regulation

[Test Vehicle]: vehicle 2

Engine: in-line four-cylinder (premium gasoline-powered with a supercharger)

Displacement: 1998 cc

Injection mode: multi point injection

Transmission: automatic transmission

Exhaust-gas purifying system: ternary catalyst, air/fuel feedback control system

Adopted to 2000 Exhaust Gas Emission Regulation

(Exhaust gas test)

An exhaust gas test was carried out using the above vehicles by measuring the emissions of CO and NOx contained in the exhaust gas, in accordance with the technical guideline of the 10/15 mode exhaust emissions measurement for gasoline-powered automobiles supervised by Ministry of Land, Infrastructure, and Transport Japan.

(Fuel consumption test)

A fuel consumption test was carried out using the above vehicles by measuring the fuel consumption in accordance with the 10/15 mode fuel consumption test procedures for gasoline-powered automobiles supervised by Ministry of Land, Infrastructure, and Transport Japan.

As set forth in Tables 4 and 6, it is confirmed that the gasolines of the present invention (Examples 3 to 10) comprising biomass-originating base oils are contributive to diversification of fuel sources and

prohibition of an increase in life cycle CO_2 and can achieve excellent acceleration performance and fuel consumption and reduced exhaust gas (CO, NOx) level.

Table 1

		Example 1	Comparative Example 1
Catalyst		Catalyst A	Catalyst B
Oxygen content (mass%, on the basis of the total mass of hydrotreated oil)		<0.2	0.4
Sulfur content (mass%, on the basis of the total mass of hydrotreated oil)		<0.2	<0.2
Yield (mass%, on the basis of feedstock)	C1−C4 (fraction of a boiling point of 80°C or lower)	5.2	3.8
	Naphtha (fraction of a boiling point of 80 to 135°C)	42.5	11.5
	Kerosene (fraction of a boiling point of 135 to 250°C)	51.7	37.7
	Gas oil (fraction of a boiling point of 250 to 350°C)	0.6	47.0
Oxygen content of fraction of a boiling point of 80 to 135°C (mass%, on the basis of the total mass of fraction of a boiling point of 80 to 135°C)		<0.2	<0.2
Normal paraffin content of fraction of a boiling point of 80 to 135°C (mass%, on the basis of the total mass of fraction of a boiling point of 80 to 135°C)		21.0	35.1

Table 2

		Example 2	Comparative Example 2
Catalyst		Catalyst C	Catalyst D
Oxygen content (mass%, on the basis of the total mass of hydrotreated oil)		<0.2	0.2
Sulfur content (mass%, on the basis of the total mass of hydrotreated oil)		2.1	4.6
Yield (mass%, on the basis of feedstock)	C1−C4 (fraction of a boiling point of 80°C or lower)	4.3	3.1
	Naphtha (fraction of a boiling point of 80 to 135°C)	35.4	9.6
	Kerosene (fraction of a boiling point of 135 to 250°C)	50.9	33.5
	Gas oil (fraction of a boiling point of 250 to 350°C)	9.4	53.8
Oxygen content of fraction of a boiling point of 80 to 135°C (mass%, on the basis of the total mass of fraction of a boiling point of 80 to 135°C)		<0.2	<0.2
Sulfur content of fraction of a boiling point of 80 to 135°C (mass%, on the basis of the total mass of fraction of a boiling point of 80 to 135°C)		1.4	3.0
Normal paraffin content of fraction of a boiling point of 80 to 135°C (mass%, on the basis of the total mass of fraction of a boiling point of 80 to 135°C)		25.1	37.2

Table 3

			Example 3	Example 4	Example 5	Example 6	Comparative Example 3	Comparative Example 4
Octane number	Research method (RON)		90.2	95.2	90.1	95.0	80.0	90.2
	Motor method (MON)		81.8	86.1	82.1	85.3	73.9	81.3
Sulfur		mass ppm	5	4	3	5	2	4
Lead		g/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Distillation characteristics	IBP	℃	33.5	31.0	33.0	31.5	31.5	31.5
	T10	℃	53.0	51.0	49.0	50.5	47.0	51.5
	T30	℃	70.0	68.5	68.5	61.5	67.5	71.5
	T50	℃	91.0	93.0	93.5	90.0	94.0	97.5
	T70	℃	112.5	124.0	119.0	117.0	113.0	123.5
	T90	℃	141.5	163.5	160.0	154.0	148.5	158.0
	EP	℃	169.5	189.5	182.5	187.5	174.0	189.0
Reid vapor pressure	@37.8℃	kPa	64.5	64.0	64.5	65.0	65.0	63.5
Density	@15℃	g/cm^3	0.7305	0.7385	0.7284	0.7402	0.6875	0.7339
Oxidation stability		min	>1440	>1440	>1440	>1440	>1440	>1440
Corrosion to copper			1a	1a	1a	1a	1a	1a
Existent gum content	Washed	mg/100ml	0	0	0	0	0	0
	Unwashed	mg/100ml	0	0	0	0	0	0
Benzene		vol.%	0.4	0.4	0.4	0.5	0.4	0.4
Composition analysis	Aromatic	vol.%	23.8	26.8	23.4	28.1	5.1	27.1
	Olefin	vol.%	10.5	11.6	9.0	17.3	12.5	15.8
Kerosene		vol.%	<1	<1	<1	<1	<1	<1
Manganese		mass ppm	<1	<1	<1	<1	<1	<1
Iron		mass ppm	<1	<1	<1	<1	<1	<1
Sodium		mass ppm	<1	<1	<1	<1	<1	<1
Potassium		mass ppm	<1	<1	<1	<1	<1	<1
Phosphorus		mass ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table 4

		Example 3	Example 4	Example 5	Example 6	Comparative Example 3	Comparative Example 4
Biomass-originating base oil content	vol.%	10	15	10	13	0	55
		passed	passed	passed	passed	not paased	passed
Vegetable oil-originating base oil content	vol.%	10	12	10	10	0	55
		passed	passed	passed	passed	not paased	passed
Acceleration time	second	7.8	7.8	7.8	7.9	9.1	7.9
		excellent	excellent	excellent	excellent	poor	excellent
Carbon monoxide (CO) emissions	g/km	0.04	0.03	0.04	0.03	0.15	0.04
		excellent	excellent	excellent	excellent	increased	excellent
Nitrogen oxide (NOx) emissions	g/km	0.02	0.03	0.02	0.03	0.08	0.03
		excellent	excellent	excellent	excellent	increased	excellent
Fuel consumption	km/L	12.0	11.9	11.9	12.1	11.1	12.0
		excellent	excellent	excellent	excellent	poor	excellent

Table 5

			Example 7	Example 8	Example 9	Example 10	Comparative Example 5	Comparative Example 6
Octane number	Research method (RON)		100.1	100.0	100.1	100.2	88.5	99.6
	Motor method (MON)		89.0	88.7	88.8	88.6	79.8	87.8
Sulfur		mass ppm	3	4	3	2	3	3
Lead		g/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Distillation characteristics	IBP	℃	34.0	33.0	33.5	32.5	31.0	32.5
	T10	℃	52.0	52.5	51.5	52.0	42.0	49.0
	T30	℃	69.5	62.5	67.5	68.5	60.0	64.0
	T50	℃	95.0	92.0	93.0	93.5	83.0	93.0
	T70	℃	122.0	111.0	114.5	114.5	106.0	121.0
	T90	℃	162.5	138.5	152.0	155.5	138.0	142.0
	EP	℃	178.5	181.0	187.5	179.5	171.0	175.5
Reid vapor pressure	@37.8℃	kPa	64.5	65.0	63.5	64.0	73.5	62.5
Density	@15℃	g/cm^3	0.7474	0.7492	0.7468	0.7488	0.6985	0.7520
Oxidation stability		min	>1440	>1440	>1440	>1440	>1440	>1440
Corrosion to copper			1a	1a	1a	1a	1a	1a
Existent gum content	Washed	mg/100ml	0	0	0	0	0	0
	Unwashed	mg/100ml	15	15	15	15	15	12
Benzene		vol.%	0.4	0.3	0.4	0.2	0.1	0.4
Composition analysis	Aromatic	vol.%	39.8	36.7	38.8	34.5	11.0	41.5
	Olefin	vol.%	17.2	18.8	19.6	17.3	18.9	15.2
Kerosene		vol.%	<1	<1	<1	<1	<1	<1
Manganese		mass ppm	<1	<1	<1	<1	<1	<1
Iron		mass ppm	<1	<1	<1	<1	<1	<1
Sodium		mass ppm	<1	<1	<1	<1	<1	<1
Potassium		mass ppm	<1	<1	<1	<1	<1	<1
Phosphorus		mass ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Table 6

		Example 7	Example 8	Example 9	Example 10	Comparative Example 5	Comparative Example 6
Biomass-originating base oil content	vol.%	5	8	5	10	40	0
		passed	passed	passed	passed	passed	not passed
Vegetable oil-originating base oil content	vol.%	5	5	5	7	40	0
		passed	passed	passed	passed	passed	not passed
Acceleration time	second	5.4	5.6	5.4	5.5	6.8	5.6
		excellent	excellent	excellent	excellent	poor	excellent
Carbon monoxide (CO) emissions	g/km	0.02	0.01	0.02	0.01	0.04	0.02
		excellent	excellent	excellent	excellent	increased	excellent
Nitrogen oxide (NOx) emissions	g/km	0.02	0.03	0.02	0.03	0.06	0.03
		excellent	excellent	excellent	excellent	increased	excellent
Fuel consumption	km/L	10.0	9.9	10.1	9.9	9.3	10.0
		excellent	excellent	excellent	excellent	poor	excellent

Claims

1. A process for hydrotreating a feedstock, comprising bringing the feedstock into contact with a catalyst in the presence of hydrogen, the feedstock containing an oxygen-containing compound, the catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Group 8 elements of the periodic table.

2. A process for hydrotreating a feedstock, comprising bringing the feedstock into contact with a catalyst in the presence of hydrogen, the feedstock containing an oxygen-containing compound and a sulfur-containing compound, the catalyst comprising a support containing a crystalline metallosilicate and one or more types of metals selected from the Groups 6A and 8 elements of the periodic table.

3. The process according to claim 1 or 2, wherein the feedstock is contacted with the catalyst under such conditions that the oxygen content and normal paraffin content of the fraction in a boiling point range of 80 to 135°C of the resulting hydrotreated oil are 0.2 percent by mass or less and 30 percent by mass or less, respectively.

4. The process according to claim 1 or 3, wherein the oxygen and sulfur contents of the feedstock are from 0.1 to 15 percent by mass and 50 ppm by mass or less, respectively on the basis of the total mass of the feedstock.

5. The process according to claim 2 or 3, wherein the oxygen and sulfur contents of the feedstock are from 0.1 to 15 percent by mass and 50 ppm by mass or less, respectively on the basis of the total mass of the feedstock.

6. The process according to any one of claims 1 to 5, wherein the oxygen-containing hydrocarbon compound is a fat component originating from an animal or vegetable oil.

7. The process according to any one of claims 1 to 6, wherein the ratio of the compound having a triglyceride structure in the oxygen-containing hydrocarbon compound is 90 percent by mole or more.

8. The process according to any one of claims 1 to 7, wherein the Group 8 elements contained in the catalyst are one or more metals selected from Pd, Pt, Rh, Ir, Au and Ni.

9. The process according to any one of claims 2 to 6, wherein the Group 6A elements contained in the catalyst are one or more metals selected from Co, Mo

and Ni.

10. The process according to any one of claims 1 to 9, wherein the crystalline metallosilicate has a structure of faujasite type.

11. The process according to any one of claims 1 to 10, wherein the crystalline metallosilicate is an ultra-stable Y type zeolite having a molar ratio of the silica to the alumina (silica/alumina) within the range of 10 to 100.

12. An environment friendly gasoline base oil, comprising a fraction with a boiling point range of 25 to 220°C of the hydrotreated oil produced by the process according to any one of claims 1 to 11.

13. The environment friendly gasoline base oil according to claim 12, wherein the base oil has an oxygen content of 0.2 percent by mass or less and a normal paraffin content of 30 percent by mass or less.

14. An unleaded gasoline composition comprising the environment friendly gasoline base oil according to claim 12 or 13.

15. The unleaded gasoline composition according to claim 14, wherein the composition has a research octane number of 89.0 or greater and less than 96.0 and a sulfur content of 10 ppm by mass or less.

16. The unleaded gasoline composition according

to claim 14, wherein the composition has a research octane number of 96.0 or greater and a sulfur content of 10 ppm by mass or less.

17. The unleaded gasoline composition according to any one of claims 14 to 16, wherein the composition has a 10% distillation temperature of 70°C or lower, a 50% distillation temperature of 75°C or higher and 110°C or lower, a 90% distillation temperature of 180°C or lower, an end point of 220°C or lower, a vapor pressure (37.8°C) of 44 kPa or greater and 93 kPa or less, a density (15°C) of 0.783 g/cm^3 or less, an oxidation stability of 240 minutes or longer, a copper corrosion (50°C, 3 hours) of 1 or less, a washed existent gum content of 5 mg/100 ml or less, an unwashed existent gum content of 20 mg/100 ml or less and a benzene content of 1 percent by volume or less.

18. The unleaded gasoline composition according to any one of claims 14 to 17, wherein the composition has an aromatic content of 45 percent by volume or less and an olefin content of 35 percent by volume or less.

19. The unleaded gasoline composition according to any one of claims 14 to 18, wherein the composition has a manganese content of 2 ppm by mass or less, an iron content of 2 ppm by mass or less, a sodium content of 2 ppm by mass or less, a potassium content of 2 ppm

by mass or less and a phosphorus content of 2 ppm by mass or less.

20. The unleaded gasoline composition according to any one of claims 14 to 19, wherein the composition contains an anti-oxidant and a metal deactivator.

21. The unleaded gasoline composition according to any one of claims 14 to 20, wherein the composition contains a detergent-dispersant.

22. The unleaded gasoline composition according to any one of claims 14 to 21, wherein the composition contains a friction modifier.