



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 686 166 A1**

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

(43) Date of publication:
02.08.2006 Bulletin 2006/31

(21) Application number: **04793223.1**

(22) Date of filing: **29.10.2004**

(51) Int Cl.:
C10L 1/06 ^(2006.01) **C10L 1/00** ^(2006.01)
C10G 29/04 ^(2006.01) **C10G 53/08** ^(2006.01)
C10G 53/10 ^(2006.01) **C10G 55/06** ^(2006.01)

(86) International application number:
PCT/JP2004/016115

(87) International publication number:
WO 2005/044959 (19.05.2005 Gazette 2005/20)

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **07.11.2003 JP 2003378503**
07.06.2004 JP 2004168365

(71) Applicant: **JAPAN ENERGY CORPORATION**
Tokyo 105-0001 (JP)

(72) Inventors:
• **ARAKI, Yasuhiro,**
c/o Japan Energy Corporation
Toda-shi, Saitama 3350026 (JP)

• **ISHIDA, Katsuaki,**
c/o Japan Energy Corporation
Toda-shi, Saitama 3350026 (JP)

(74) Representative: **Forstmeyer, Dietmar et al**
BOETERS & LIECK
Oberanger 32
80331 München (DE)

(54) **LEAD-FREE GASOLINE COMPOSITION AND METHOD FOR PRODUCTION THEREOF**

(57) An unleaded gasoline composition having a sulfur content of 1 mass ppm or less and exhibiting sufficient driving performance and a method thereof are provided.

A method for producing an unleaded gasoline composition having a sulfur content of 1 mass ppm or less and a research method octane number of 89.0 or more, which comprises a step of subjecting a cracked naphtha fraction having a 5 vol % distillation temperature of 25°C or higher, a 95 vol % distillation temperature of 210°C or lower, an olefin content of 5 mass % or more and a diene value of 0.3 g/100 g or less to a desulfurization treatment,

and a blending step of mixing the above resultant desulfurized cracked naphtha fraction with another gasoline base materials; and an unleaded gasoline composition which has a research method octane number of 89.0 or more, a 50 vol % distillation temperature of 105°C or lower, an olefin content of 10 vol % or more, a total sulfur content of 1 mass ppm or less, and a percentage of a thiophene type sulfur compound in the total sulfur content of 50 mass % or more as sulfur.

EP 1 686 166 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to an unleaded gasoline composition with reduced harmful effects on environment and a method for producing the same. More particularly, the present invention relates to an unleaded gasoline composition having a sulfur content of 1 mass ppm or less and exhibiting sufficient driving performance, while giving due consideration to environment and to a method for producing the gasoline composition.

BACKGROUND ART

[0002] In recent years, the demand for high performance gasoline with a high driving performance is increasing along with improvement of vehicle performance. On the other hand, the environmental pollution due to vehicle fuel or exhaust gas is being highlighted as a social problem. Therefore, a vehicle fuel exhibiting small environmental impact while maintaining high performance is desired. In particular, from the viewpoint of exhaust gas purification and improvement of fuel consumption, a further reduction of the sulfur content is strongly desired.

[0003] JIS K 2202 specifies No. 1 motor gasoline with a research octane number (RON) of 96.0 or more and No.2 motor gasoline with a RON of 89.0 or more. The former gasoline is commercially supplied as high performance premium gasoline and the latter as regular gasoline. Premium gasoline is commonly manufactured by blending various gasoline base materials, mainly gasoline base materials having a 100 or greater RON such as a catalytically reformed gasoline and methyl t-butyl ether (MTBE), and another gasoline base materials having a 93 or greater RON such as alkylate gasoline and catalytically cracked gasoline.

[0004] Cracked gasoline base material manufactured by cracking heavy petroleum distillates has an advantage that it can be manufactured economically, but contains a large amount of sulfur as compared with another gasoline base materials. Consequently, a great portion of the sulfur content in gasoline products manufactured in the above-mentioned manner is derived from the cracked gasoline base material.

[0005] The sulfur content in cracked gasoline base material can be easily reduced using a known hydrotreating process in the presence of hydrogen and a catalyst under high pressure. However, since in such case the hydrotreating process hydrogenates olefins having a high RON contained in a large amount in catalytic cracked gasoline, the gasoline products obtained by blending the resulting gasoline base material cannot exhibit sufficient driving performance due to the reduced RON.

[0006] A process for continuously reducing the sulfur content in hydrocarbon oil used as a gasoline base material comprising repeating a step of causing hydrocarbon oil to come into contact with an adsorbent under specific conditions to adsorb sulfur compounds and a step of desorbing the sulfur compounds from the adsorbent by circulating hydrogen to the adsorbent, while inhibiting unnecessary reactions such as hydrogenation of olefins has been proposed (refer to Patent Document 1). However, this process of using an adsorbent cannot continuously and effectively reduce the sulfur content due to a possible adverse effect on sulfur adsorption capability of the adsorbent by specific hydrocarbons contained in the feedstocks. The process was not necessarily satisfactory.

[Patent Document 1] Japanese Patent Application Laid-open No. 2003-277768

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] Pollution-free gasoline having a low sulfur content of 1 mass ppm or less and exhibiting sufficient driving performance and a method for producing such gasoline have not been yet established. An object of the present invention is to provide an unleaded gasoline composition having a reduced sulfur content and exhibiting sufficient driving performance and a method for producing such a gasoline composition.

MEANS FOR SOLVING THE PROBLEMS

[0008] As a result of extensive studies to achieve the aforementioned object, the inventors of the present invention have found that if a cracked naphtha fraction with a low diene content is subjected to a desulfurization treatment other than hydrotreating, the sulfur content can be efficiently reduced, while maintaining a high RON, and an unleaded gasoline composition exhibiting sufficient driving performance can be obtained by using such gasoline base material obtained in said manner. This finding has led to the creation of the unleaded gasoline composition and a method for producing the same of the present invention.

[0009] Specifically, the method for producing an unleaded gasoline composition having a sulfur content of 1 mass ppm or less and a RON of 89.0 or more of the present invention comprises:

- (1) a step of subjecting a cracked naphtha fraction having a 5 vol% distillation temperature of 25°C or more, a 95 vol% distillation temperature of 210°C or less, an olefin content of 5 vol% or more, and a diene value of 0.3 g/100 g or less to a desulfurization treatment, and
- (2) a step of blending the resulting desulfurized cracked naphtha fraction with another gasoline base material.

[0010] In the above step (1), a cracked naphtha fraction with a diene value of 0.3 g/100 g or less which has been previously subjected to a diene-reducing treatment is preferably used. In other words, the method for producing an unleaded gasoline composition of the present invention preferably comprises a diene-reducing step of previously reducing the diene content of the raw oil of the cracked naphtha fraction. In this instance, the diene-reducing step preferably comprises causing the raw cracked naphtha fraction to come in contact with a catalyst containing a group 8 element in the periodic table. The diene-reducing catalyst preferably comprises at least one selected from cobalt and nickel.

[0011] Furthermore, in the desulfurization step (1) of the method for producing an unleaded gasoline composition of the present invention, the cracked naphtha fraction is preferably caused to come in contact with a porous desulfurization agent with a sulfur sorption function in the presence of hydrogen under a hydrogen partial pressure of 1 MPa or less. The porous desulfurization agent preferably contains at least one element selected from the group consisting of copper, zinc, nickel, and iron. In the blending step (2), 10-90 vol% of the desulfurized cracked naphtha fraction is preferably blended with 90-10 vol% of another gasoline base materials.

[0012] In the method for producing an unleaded gasoline composition of the present invention, in order to obtain an unleaded gasoline composition having a high octane number, for example, a RON of 93.0 or more, particularly a RON of 96.0 or more, a light cracked naphtha fraction having a 5 vol% distillation temperature of 25-43°C, a 95 vol% distillation temperature of 55-100°C, an olefin content of 5 vol% or more, and a diene value of 0.3 g/100 g or less is preferably used in the desulfurization step (1).

Such a light cracked naphtha fraction may be obtained by subjecting the cracked naphtha fraction to a diene-reducing treatment, followed by fractional distillation, fractionating the cracked naphtha fraction, followed by a diene-reducing treatment, or simultaneous fractional distillation and diene-reducing treatment.

A raw oil of cracked naphtha fraction, or a raw oil of cracked naphtha fraction subjected to a diene-reducing treatment, is preferably pretreated for increasing the molecular weight of sulfur compounds, prior to or simultaneously with the fractional distillation for obtaining a light cracked naphtha fraction. This pretreatment ensures easy reduction of the sulfur content of the light cracked naphtha fraction.

[0013] In a preferred embodiment of the method for producing an unleaded gasoline composition of the present invention, after desulfurizing such a light cracked naphtha fraction in the step (1), 10-60 vol% of the light desulfurized cracked naphtha fraction is blended with 90-40 vol% of another gasoline base materials in the step (2) to obtain an unleaded gasoline composition with a RON of 93.0 or more.

[0014] The unleaded gasoline composition of the present invention has a RON of 89.0 or more, a 50 vol% distillation temperature of 105°C or less, an olefin content of 10 vol% or more, a total sulfur content of 1 mass ppm or less, and a proportion of thiophene compounds to the total sulfur compounds of 50 mass% or more, as the sulfur content.

The unleaded gasoline composition of the present invention preferably has a RON of 93.0 or more. More preferably, the unleaded gasoline composition of the present invention contains 90.0 vol% or more of olefins having a boiling point of 35-100°C in the total olefin content and has the proportion of total of thiophene and 2-methylthiophene to the total sulfur compounds of 50 mass% or more, as the sulfur content, and/or a thiol compound content of 0.1 mass ppm or less, as the sulfur content.

EFFECTS OF THE INVENTION

[0015] Dienes are inevitably included, particularly, in cracked naphtha fractions such as catalytically cracked gasoline and various other types of cracked gasolines. If dienes are contained, the dienes are preferentially adsorbed in a porous desulfurization agent during treating with a porous desulfurization agent and the porous desulfurization agent is impaired its sulfur sorption function. On the other hand, since the present invention limits a diene value to 0.3 g/100 g or less by carrying out a treatment reducing the dienes previously, the high sulfur sorption function can be maintained for a long period of time. Specifically, an unleaded gasoline composition with a sulfur content of 1 mass ppm or less can be produced by blending a desulfurized cracked naphtha fraction, which is obtained by treating catalytically cracked gasoline, after removal of the dienes, with a porous desulfurization agent having a sulfur sorption function in the presence of a small amount of hydrogen, and another gasoline base materials with a sulfur content of 10 mass ppm or less. Since it is possible to remove thiophene compounds in cracked naphtha fractions such as catalytically cracked gasoline, light cracked naphtha fractions such as cracked naphtha fractions containing a large amount of thiophene compounds can

also be desulfurized. Moreover, since almost no olefins contained in a large amount in light cracked naphtha fractions such as catalytic cracked light gasoline are hydrogenated, a decrease in the octane number accompanying the desulfurization treatment can be avoided. Therefore, it is possible to reduce only the sulfur content to 1 mass ppm or less, while changing almost no other properties of conventional unleaded gasoline compositions.

BEST MODE FOR CARRYING OUT THE INVENTION

[0016] The present invention is a method for producing an unleaded gasoline composition having a sulfur content of 1 mass ppm or less and a research octane number of 89.0 or more comprising a desulfurization step of subjecting a cracked naphtha fraction having specific properties to a desulfurization treatment, and a blending step of mixing the resulting desulfurized cracked naphtha fraction with another gasoline base materials. Although the present invention will be discussed in the following description mainly for the case of using a fluid catalytically cracked gasoline (FCC gasoline) as the cracked naphtha fraction, the invention is by no means limited to the FCC gasoline, but various products and intermediate products obtained from petroleum refining process, petrochemical process or the like, for example, thermally cracked naphtha obtained from a thermal cracking unit, dewaxed naphtha obtained from a dewaxing plant, and cracked naphtha produced in a naphtha cracker can be used as the cracked naphtha fraction, inasmuch as the cracked naphtha fraction has a 5 vol% distillation temperature of 25°C or more, a 95 vol% distillation temperature of 210°C or less, an olefin content of 5 vol% or more, and a diene value of 0.3 g/100 g or less. Therefore, in addition to a whole cracked naphtha fraction, a light cracked naphtha fraction or a heavy cracked naphtha fraction obtained by fractional distillation of the whole cracked naphtha fraction can be used insofar as the above conditions are satisfied. The 5 vol% distillation temperature of these cracked naphtha fractions is preferably 25-130°C, and the 95 vol% distillation temperature is preferably 55-210°C. In order to use a cracked naphtha fraction with a diene value of 0.3 g/100 g or less, the cracked naphtha fraction is preferably subjected to a diene-reducing treatment described below in detail prior to the desulfurization treatment.

<Diene-reducing step>

[0017] In the method for producing the unleaded gasoline composition of the present invention, a cracked naphtha fraction such as FCC gasoline is previously subjected to a diene-reducing treatment to obtain a cracked naphtha fraction with a diene value of 0.3 g/100 g or less. A diene value of 0.1 g/100 g or less is more preferable. If the diene value is more than 0.3 g/100 g, the desulfurization performance of the porous desulfurization agent having a sulfur sorption function used in the subsequent desulfurization step is impaired, resulting in difficulty of desulfurizing sulfur compounds, particularly, thiophene compounds. A decrease of desulfurization performance can be identified by a decrease in the desulfurization rate per unit throughput or an increase in the regeneration frequency of the porous desulfurization agent for retaining a predetermined rate of desulfurization. Therefore, it is preferable to send the cracked naphtha fraction feed to the desulfurization step after pretreatment for reducing diene compounds. However, since the octane number significantly decreases if olefms are hydrogenated into paraffins in this diene-reducing step, a selective diene-reducing treatment that olefms are not hydrogenated is preferable.

[0018] The diene value used in this specification is a value measured according to the method of UOP 326-82.

The sulfur content can be reduced simultaneously with the diene content by selecting the catalyst and conditions of the diene-reducing step. The life of a porous desulfurization agent with a sorption function can be consequently extended.

[0019] As the method for reducing dienes, a method of causing a catalytically cracked naphtha fraction to come into contact with a diene-reducing catalyst in the presence of hydrogen to convert dienes into monoolefins, or to react dienes with sulfur compounds that are present together with the dienes into sulfides are preferably employed. As the diene-reducing catalyst, a catalyst containing at least one metal in group 8 of the periodic table supported on a porous inorganic carrier such as alumina is preferably used. A catalyst containing nickel or cobalt having resistance to sulfur-containing raw oils is still more preferable. The reaction conditions must be set so that the diene value in the catalytically cracked naphtha fraction can be reduced to 0.3 g/100 g or less and the olefin hydrogenation rate can be 20% or less. Here, the olefin hydrogenation rate indicates the percentage of olefm content reduction rate of the olefin content after treatment to the olefm content (100%) before the treatment.

Preferable reaction conditions when causing a catalytically cracked naphtha fraction to come in contact with a diene-reducing catalyst in the presence of hydrogen are the reaction temperature of 40-300°C, the reaction pressure of 0.0-4.0 MPa (gauge pressure), LHSV of 1.0-10.0 hr⁻¹, and H₂/oil ratio of 1-100 NL/L.

[0020] Selective hydrogenation of dienes in olefms, which has been conventionally performed in petroleum refiners, can be used in the present invention as a method for reducing dienes. Specifically, the IFP Selective Hydrogenation process, Hules Selective Hydrogenation process, and the like are preferably used (see "Petroleum Refining Processes" edited by the Japan Petroleum Institute, p. 62, Kodansha Scientific, 1998).

In the present invention, the SHU process (21st JPI Petroleum Refining Conference "Recent Progress in Petroleum

Process Technology" 37 (2002)) and CD Hydro process (NPRA 2001 Annual Meeting, AM-01-39) can also be used as the process for reducing the diene content.

<Catalytically cracked gasoline>

[0021] As mentioned above, catalytically cracked gasoline is typically used as the cracked naphtha fraction in the method for producing the unleaded gasoline composition of the present invention. Any processes known in the art can be used as the method for producing the catalytically cracked gasoline without specifically limiting catalytic cracking unit, feedstocks, and operating conditions. A catalytic cracking unit is an apparatus for obtaining high octane gasoline base materials by catalytic cracking of various petroleum fractions, which include, in addition to fractions from gas oil to vacuum gas oil, indirect desulfurization gas oil obtained from an indirect desulfurization process of heavy distillate oils, direct desulfurization fuel oil obtained from direct desulfurization process of heavy distillate oils and atmospheric residue, and the like using a catalyst comprising amorphous silica-alumina, zeolite, or the like. For example, fluid catalytic cracking processes such as a UOP catalytic cracking process, Flexicracking process, Ultra Orthoflow process, and Texaco fluid catalytic cracking process; residue fluid catalytic cracking processes such as an RCC process and HOC process; and the like, described in "New Petroleum Refining Processes" edited by the Japan Petroleum Institute can be given.

[0022] As the feedstock of catalytic cracking units for obtaining cracked naphtha fractions with a reduced sulfur content, petroleum fractions from gas oil to vacuum gas oil can be preferably used. Particularly fractions in which the sulfur content has been subjected to a reducing treatment by hydrotreating to preferably 4,000 mass ppm or less, more preferably 2,000 mass ppm or less, still more preferably 1,000 mass ppm or less, and particularly preferably 500 mass ppm or less, can be used.

<Desulfurization step>

[0023] In the desulfurization step in the method for producing the unleaded gasoline composition of the present invention, a cracked naphtha fraction with a diene value of 0.3 g/100 g or less is desulfurized to obtain a desulfurized cracked naphtha fraction to be sent to the next blending step. In this step, the sulfur content of the naphtha fraction is reduced preferably to 2 mass ppm or less, more preferably to 1 mass ppm or less, and still more preferably to 0.5 mass ppm or less. Thiophenes are compounds that tend to most hardly desulfurize among the sulfur compounds in the desulfurization step. Therefore, the proportion of thiophenes to the total sulfur compounds in the desulfurized cracked naphtha fraction is preferably 50 mass% or more, and more preferably 70 mass% or more, as sulfur. Thiophene compounds here are meant sulfur compounds having a thiophene skeleton in the molecule such as thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and the like. The olefin content in the desulfurized catalytically cracked gasoline is preferably 5-60 vol%, and particularly preferably 20-40 vol%.

[0024] As the method of desulfurization in the desulfurization step, a method of causing a cracked naphtha fraction to come in contact with a desulfurization agent having a sorption function in the presence of hydrogen is preferable. The hydrotreatment of cracked naphtha fractions in the presence of a hydrodesulfurization catalyst and hydrogen is unsuitable due to insufficient desulfurization, because not only olefins easily hydrogenated to decrease the RON of the resulting gasoline base material, but also hydrogen sulfide produced by hydrodesulfurization easily reacts with olefins to reproduce thiols. Use of a desulfurization agent with a sorption function is preferable, because the sulfur removed from an organic sulfur compound is immobilized on the desulfurization agent and inhibited from reacting with olefins not to reproduce thiols.

[0025] There are no specific limitations to the desulfurization agent with a sulfur sorption function when using the method for causing a cracked naphtha fraction to come in contact with the desulfurization agent, insofar as such a desulfurization agent has a function of sorbing sulfur compounds. A porous desulfurization agent comprising at least one metal selected from copper, zinc, nickel, and iron is preferably used. A preferable desulfurization agent contains 0.5-85 mass%, particularly 1-80 mass% of a metal component such as copper. Although the method of preparing the desulfurization agent not specifically limited, a method of impregnating a porous carrier such as alumina with a metal component such as copper and baking the porous carrier with the metal component supported thereon, a method of coprecipitating a metal component such as copper together with another component such as aluminum, forming the resulting solid, and baking the formed product or the like can be given as a preferable method. The formed and baked product may be further impregnated with a metal component to cause the metal component to be supported thereon, followed by baking. The desulfurization agent obtained by baking may be used as is or after treatment in a hydrogen atmosphere. The specific surface area of the desulfurization agent is preferably 30 m²/g or more, and particularly preferably 50-600 m²/g. Although there are no specific limitations to the composition of the desulfurization agent and the method for manufacturing the same, the desulfurization agents disclosed in Japanese Patent No. 3324746, Japanese Patent No. 3230864, or Japanese Patent Application Laid-open No. 11-61154 can be given as a preferable desulfurization agent.

[0026] The porous desulfurization agent having a sulfur sorption function used in the present invention is an agent

that can immobilize sulfur atoms in organic sulfur compounds on the desulfurization agent and can release hydrocarbon residues in the organic sulfur compounds by cleaving the carbon-sulfur bonds in the organic sulfur compounds. When the hydrocarbon residues are released, hydrogen that is present in the system bonds to the carbon atom from which a sulfur atom has dissociated by cleavage of the C-S bond. Therefore, the hydrocarbon compounds can be obtained as a product resulting from removal of sulfur atoms from the organic sulfur compounds. The hydrocarbon compounds obtained by removing sulfur atoms may be further reacted by hydrogenation, isomerization, decomposition, and the like. On the other hand, since sulfur is immobilized on the desulfurization agent, no sulfur compound such as hydrogen sulfide that is produced in the hydrotreating process is produced as a product.

[0027] Either a batch process or a continuous process can be employed for the desulfurization treatment. A method of continuously processing cracked naphtha fraction through a fixed bed desulfurization reactor loaded with a desulfurization agent is preferable since the desulfurized cracked naphtha fraction obtained may be simply separated from the desulfurization agent. The desulfurization temperature can be selected from a range of 0-400°C, and preferably 20-380°C. In order to promote desulfurization of thiophenes which are desulfurized only with difficulty by merely being brought into contact with a desulfurization agent, the desulfurization treatment may be carried out in the presence of hydrogen. However, the partial pressure of hydrogen should preferably be less than 1 MPa, and more preferably less than 0.6 MPa, in order to avoid hydrogenation of olefins, which results in a decrease of RON of the resulting gasoline base material. When the cracked naphtha fraction is desulfurized by being brought into contact with a desulfurization agent in a fixed bed continuous system, LHSV is preferably selected from a range of 0.01-10000 hr⁻¹.

[0028] A gasoline base material with a high octane number is preferable as a gasoline base material to be used during manufacturing premium gasoline. The gasoline base material with a high octane number is also preferable for producing regular gasoline due to its capability of increasing blending flexibility. In addition, it is possible to fractionate a cracked naphtha fraction to obtain a light cracked naphtha fraction having a comparatively high octane number, and the cracked naphtha fraction is subjected to the diene-reducing treatment and desulfurization treatment, and blend the resulting desulfurized product with another gasoline base material to obtain the unleaded gasoline composition of the present invention.

[0029] The light cracked naphtha fraction after fractional distillation and diene-reducing treatment preferably has a 5 vol% distillation temperature of 25-43°C, a 95 vol% distillation temperature of 55-100°C, an olefin content of 5 vol% or more, and a diene value of 0.3 g/100 g or less. The light cracked naphtha fraction may be obtained by fractional distillation after the diene-reducing treatment, by a diene-reducing treatment after fractional distillation, or by a simultaneous fractional distillation and diene-reducing treatment. A treatment for increasing the molecular weight of sulfur compounds prior to or during the fractional distillation can reduce the sulfur content of the light cracked naphtha fraction in a simple operation of causing the sulfur compounds with an increased molecular weight to move into heavy cracked naphtha fractions having a high boiling point. The above steps of fractional distillation and pretreatment for increasing the molecular weight of sulfur compounds will be discussed below in more detail.

<Fractional distillation step>

[0030] In the fractional distillation step in the method for producing the unleaded gasoline composition of the present invention, catalytically cracked gasoline is fractionated to obtain a light cracked naphtha fraction such as a catalytically cracked light gasoline having a 5 vol% distillation temperature of 25.0-43.0°C and a 95 vol% distillation temperature of 55.0-100.0°C. If the 5 vol% distillation temperature is less than 25.0°C, the vapor pressure of the resulting unleaded gasoline composition may become high. If the 95 vol% distillation temperature is more than 80.0°C, particularly more than 100.0°C, the sulfur content of the catalytically cracked light gasoline after desulfurization may become high. If the 5 vol% distillation temperature is more than 43.0°C or the 95 vol% distillation temperature is less than 55.0°C, adjusting the distillation properties of the unleaded gasoline composition will be difficult and the yield of the catalytically cracked light gasoline obtained in the fractional distillation step may be decreased, which results in a cost increase of the unleaded gasoline composition.

[0031] The catalytically cracked light gasoline obtained in the fractional distillation step preferably contains thiophene compounds in an amount of 0.1-50 mass ppm, as the sulfur content. The content of 20 mass ppm or less is preferable, 10 mass ppm or less is particularly preferable. Thiophenes are sulfur compounds which are most likely to remain undesulfurized in the desulfurized catalytically cracked light gasoline obtained in the subsequent desulfurization step. If the catalytically cracked light gasoline obtained in the fractional distillation step contains the thiophenes in excess of 50 mass ppm as the sulfur content, the desulfurization agent unpreferably exhibits a shortened operation period in the desulfurization step. Reducing thiophene compounds in the catalytically cracked light gasoline obtained in the fractional distillation step to less than 0.1 mass ppm as the sulfur content, is undesirable, because the yield of the catalytically cracked light gasoline is unduly reduced.

[0032] When a catalytically cracked gasoline is fractionated to obtain a light cracked naphtha fraction in the fractional distillation step, a comparatively heavy cracked naphtha fraction is also produced as a matter of course. The heavy

cracked naphtha fraction is by no means rejected in the present invention. Such a fraction can be suitably used for producing the unleaded gasoline composition of the present invention, particularly that having a comparatively low octane number at a low cost, inasmuch as the fraction satisfies the conditions of a 5 vol% distillation temperature of 25°C or more, and preferably 25-130°C, a 95 vol% distillation temperature of 210°C or less, and preferably 55-210°C, an olefin content of 5 mass% or more, and a diene value of 0.3 g/100 g or less. Usually, catalytically cracked heavy gasoline has a larger sulfur content than catalytically cracked light gasoline. In particular, when the sulfur content of the catalytically cracked heavy gasoline is 50 mass ppm or more, a treatment of such a gasoline after removing only dienes with a desulfurization agent having a sorption function in the presence of hydrogen unduly reduces the life of the desulfurization agent. In addition, catalytically cracked heavy gasoline has a comparatively less olefin content. Therefore, the catalytically cracked heavy gasoline can be desulfurized by hydrodesulfurization in the presence of high pressure hydrogen to a sulfur content of about 5 mass ppm without unduly reducing the octane number. Therefore, it is preferable to desulfurize catalytically cracked heavy gasoline by a treatment with a desulfurization agent having a sorption function in the presence of hydrogen after reducing the sulfur content to 20 mass ppm or less, preferably 10 mass ppm or less, and more preferably 5 mass ppm or less, by hydrodesulfurization in the presence of high pressure hydrogen while controlling the olefin hydrogenation rate to 20% or less, and preferably 10% or less. In this instance, the diene content can be reduced simultaneously with desulfurization during hydrodesulfurization. Previously reducing the diene content is preferable to inhibit an adverse effect on the hydrodesulfurization catalyst and hydrodesulfurization apparatus due to the diene polymerization.

[0033] Thiophene compounds, particularly thiophene compounds having an alkyl group at the 2nd position, are sulfur compounds which are most likely to remain undesulfurized in the desulfurized catalytically cracked light gasoline obtained in the desulfurization step. Major thiophene compounds that are present in catalytically cracked light gasoline include thiophene, 2-methylthiophene, and 3-methylthiophene. Among these, the thiophene compound having an alkyl group at the 2nd position is 2-methylthiophene. Therefore, the amount of 2-methylthiophene is preferably reduced in the fractional distillation step in advance. For this reason, in the fractional distillation step the 95 vol% distillation temperature is preferably controlled to 100°C or less, more preferably 85.0°C or less, and particularly preferably 75°C or less. If the 95 vol% distillation temperature during fractional distillation is reduced to 75°C or less, the catalytically cracked light gasoline contains not only almost no 2-methylthiophene, but also almost no 3-methylthiophene. In this case, a major thiophene compound contained in the catalytically cracked light gasoline is thiophene. Accordingly, when the 95 vol% distillation temperature is controlled to 75°C or less in fractional distillation step, the thiophene compound which is most likely to remain in the desulfurized catalytically cracked light gasoline obtained in the desulfurization step is thiophene.

<Pretreatment for increasing molecular weight of sulfur compound>

[0034] The catalytically cracked gasoline to be subjected to the fractional distillation step is preferably pretreated for increasing the molecular weight of sulfur compounds therein, and then fed to the fractional distillation step, or such a pretreatment for increasing the molecular weight of sulfur compounds may be carried out simultaneously with the fractional distillation. Since the boiling point of sulfur compounds increases due to selectively increasing the molecular weight of the sulfur compounds such as thiols, the sulfur compounds can be shifted into catalytically cracked heavy gasoline in the fractional distillation step, whereby it is possible to reduce the sulfur content of catalytically cracked light gasoline obtained in the fractional distillation step. Specifically, the content of thiols (as sulfur) in the catalytically cracked light gasoline is more preferably 0.1 mass ppm or less.

[0035] Sweetening is conventionally carried out in petroleum refining for treating thiols to deodorize the petroleum products. Known methods for converting thiols into disulfides by oxidation and oxidative extraction can be applied as a means for increasing the molecular weight of sulfur compounds in the present invention. Specifically, the Merox process, Doctor process, and the like can be preferably used (see The Petroleum Refining Technical Manual, 3rd Edition, Sangyo Tosho Publishing Co., Ltd., 1981).

[0036] A method of reacting sulfur compounds in cracked naphtha fractions with olefins can be also preferably used as a method for increasing the molecular weight of the sulfur compounds in the present invention. As specific examples, a method of reacting thiols with olefins (cf. Japanese Patent Application Laid-open No. 2001-55584) and a method of reacting thiols and thiophenes with olefins (cf. "Production of Low Sulfur Gasoline and Diesel Fuels: Tier 2 and Beyond" Petroleum Refining Technology Seminar August 2001, 11-18) can be given. It is particularly preferable to use a process that can increase the molecular weight of sulfur compounds simultaneously with diene-reducing treatment. Specifically, the aforementioned SHU process is preferably used. It is still more preferable to use a process that can increase the molecular weight of sulfur compounds simultaneously with diene-reducing treatment during fractional distillation. Specifically, the aforementioned CD Hydro process is preferably used.

<Another gasoline base materials used in blending step>

[0037] Known gasoline base materials can be used in the blending step as another gasoline base material. Such gasoline base materials include catalytically reformed gasoline, alkylate gasoline, desulfurized straight run naphtha, isomerized gasoline, naphtha fraction produced in a naphtha cracker, toluene, xylene, and oxygen-containing gasoline base materials such as MTBE, ethyl t-butyl ether (ETBE), t-amyl ethyl ether (TAEE), ethanol, methanol, and the like. The sulfur content of such another gasoline base material used in the blending step is preferably 10 mass ppm or less, more preferably 3 mass ppm or less, still more preferably 1 mass ppm or less, and particularly preferably 0.5 mass ppm or less. If the sulfur content of a gasoline base material is more than 10 mass ppm, the amount of that gasoline base material used in the blending step is unpreferably restricted.

[0038] Preferable amounts of the gasoline base materials will be described for each research octane number. For example, a preferable proportion of blending stocks to produce an unleaded gasoline composition having a RON of 96-102 is 25-80 vol%, and particularly 30-50 vol% of desulfurized cracked naphtha fraction, 25-50 vol%, and particularly 30-45 vol% of catalytically reformed gasoline, and 10-40 vol%, and particularly 15-30 vol% of alkylate gasoline.

A preferable proportion of blending stocks to produce an unleaded gasoline composition having a RON of 93-96 is 50-90 vol%, and particularly 60-80 vol% of desulfurized cracked naphtha fraction, 5-35 vol%, and particularly 10-25 vol% of catalytically reformed gasoline, and 10-25 vol%, and particularly 5-15 vol% of alkylate gasoline.

A preferable proportion of blending stocks to produce an unleaded gasoline composition having a RON of 89-93 is 55-90 vol%, and particularly 65-85 vol% of desulfurized cracked naphtha fraction, 0-20 vol%, and particularly 5-15 vol% of catalytically reformed gasoline, and 0-15 vol%, and particularly 0-10 vol% of alkylate gasoline.

<Additives>

[0039] One or more additives for fuel oil known in the art may be optionally added to the gasoline composition of the present invention. Although the amount of the additives may be appropriately determined, usually it is preferable that the total amount of the additives be limited to 0.1 mass% or less. Examples of fuel oil additives that can be used in the gasoline composition of the present invention include antioxidants such as a phenol antioxidant and an amine antioxidant; metal deactivators such as a Schiff-type compound and a thioamide-type compound; surface ignition inhibitors such as an organic phosphorus compound; detergent-dispersants such as succinimide, polyalkylamine, and polyether amine; deicing agents such as a polyhydric alcohol or its ether; combustion improvers such as an alkaline metal salt or alkaline earth metal salt of organic acid, a sulfate of more alcohol; antistatic agents such as an anionic surfactant, cationic surfactant, and amphoteric surfactant; and coloring agents such as an azo dye.

<Unleaded gasoline composition>

[0040] The unleaded gasoline composition of the present invention has a RON of 89.0 or more, a 50 vol% distillation temperature of 105°C or less, an olefin content of 10 vol% or more, a total sulfur content of 1 mass ppm or less, and a proportion of thiophene compounds in the total sulfur compounds of 50-100 mass%, as the sulfur content. Preferably, lower limits of the RON are 93.0 or more, particularly 96.0 or more, and upper limits usually not more than 102.0, the amount of olefins having a boiling point of 35-100°C in the total olefin is 90.0 vol% or more, and the proportion of the total amount of thiophene and 2-methylthiophene in the total sulfur compounds is 50 mass% or more, and preferably 70 mass% or more, as the sulfur content, and the content of thiol compounds in the gasoline composition is 0.1 mass ppm or less, as the sulfur content.

[0041] The present invention is described in more detail by way of examples. However, the following examples should not be construed as limiting the present invention.

Preparation of gasoline base material 1

[0042] 5 cm³ of a catalyst composed of alumina on which 20 mass% of nickel is supported was sulfurized at 300°C using a solution of 2 mass% of dimethyl disulfide dissolved in n-heptane. Catalytically cracked gasoline A obtained by fluid catalytic cracking of a feed oil containing hydrotreated vacuum gas oil fraction obtained from a Middle East crude oil as a major component was subjected to diene-reducing treatment under the conditions of a reaction temperature of 250°C, atmospheric pressure, liquid hourly space velocity (LHSV) of 4 hr⁻¹, and H₂/Oil ratio of 340 NL/L, to obtain catalytically cracked gasoline B. 5 cm³ of copper-zinc-aluminum complex oxide (Cu: 35 mass%, Zn: 35 mass%, Al: 5 mass%) prepared by the coprecipitation method was loaded in a reactor tube and subjected to a reduction treatment by circulating hydrogen gas at a rate of 5 cm³/min and a temperature of 200°C for 16 hours. Then, the catalytically cracked gasoline B was fed to the reactor tube for 20 hours under the conditions of a reaction temperature of 100°C, atmospheric pressure, LHSV of 2.0 hr⁻¹, and H₂/Oil ratio of 0.06 NL/L to obtain desulfurized catalytically cracked gasoline

EP 1 686 166 A1

C which was desulfurized by the desulfurization agent with a sorption function. Properties of the catalytically cracked gasoline A, catalytically cracked gasoline B, and desulfurized catalytically cracked gasoline C are shown in Table 1.

[0043] The density, vapor pressure, distillation characteristics, and diene value were measured according to the methods of JIS K 2249, JIS K 2258, JIS K 2254, and UOP 326-82 respectively. The sulfur content was measured according to the method of ASTM D5453 (ultraviolet fluorescence method). The content of sulfur compounds (as sulfur) was measured by gas chromatography using a gas chromatographic device (manufactured by Shimadzu Corp.) equipped with a sulfur chemiluminescence detector (manufactured by ANTEK) which selectively detects and determines the amount of sulfur compounds by chemiluminescence. The hydrocarbon component composition and RON were measured by gas chromatography using the PIONA analyzer manufactured by Hewlett Packard.

[0044]

[Table 1]

		Catalytically cracked gasoline A	Catalytically cracked gasoline B	Desulfurized catalytically cracked gasoline C
	Density (15°C) [g/cm ³]	0.7330	0.7326	0.7319
	Vapor pressure (37.8°C) [kPa]	73.0	70.0	70.0
	Hydrocarbon composition [vol%]			
	Saturated component	53.8	53.8	53.5
	Olefin component	23.2	23.0	23.2
	Aromatic component	23.0	23.2	23.3
	RON	91.3	91.3	91.3
	Diene value [g/100g]	0.6	0.1	<0.1
	Sulfur content [mass ppm]	16.2	5.0	0.2
	Sulfur compounds content [as a sulfur, mass ppm]			
	Thiophenes	3.7	3.8	0.2
	Benzothiophenes	1.0	0.9	0.0
	Thiols	10.7	0.1	0.0
	Sulfides	0.7	0.1	0.0
	Disulfides		0.0	0.0

(continued)

Distillation properties [°C]				
5 10 15	Initial boiling point	31.5	31.5	33.5
	5 vol% distillation temp	44.0	45.0	46.0
	10 vol% distillation temp	48.0	49.0	49.5
	50 vol% distillation temp	92.0	93.0	93.0
	90 vol% distillation temp	166.0	165.5	166.0
	95 vol% distillation temp	178.0	177.5	177.5
	End point	190.0	189.5	191.0

[0045] Catalytically cracked gasoline A was found to have a diene value of 0.6 g/100 g, whereas the diene value of catalytically cracked gasoline B was 0.1 g/100 g, confirming sufficient removal of dienes. Catalytically cracked gasoline B containing 5.0 mass ppm of sulfur was desulfurized by the treatment with the desulfurization agent into desulfurized catalytically cracked gasoline C with a sulfur content of 0.2 mass ppm. The resulting desulfurized catalytically cracked gasoline C contained 0.2 mass ppm of thiophenes, but did not contain other sulfur compounds.

Preparation of gasoline base material 2

[0046] In the same manner as in the preparation of gasoline base material 1, catalytically cracked light gasoline E was obtained by fractionating another lot of a catalytically cracked gasoline D from Middle East crude oil into a light fraction and a heavy fraction. The catalytically cracked light gasoline E was subjected to a diene-reducing treatment under the same conditions as in the preparation of gasoline base material 1, except that the reaction temperature was 200°C and LHSV was 2 hr⁻¹, to obtain catalytically cracked light gasoline F. The catalytically cracked light gasoline F was desulfurized exactly in the same manner under the same conditions as in the preparation of gasoline base material 1 to obtain desulfurized catalytically cracked light gasoline G. Properties of the catalytically cracked gasoline D, catalytically cracked light gasoline E, catalytically cracked light gasoline F, and desulfurized catalytically cracked light gasoline G are shown in Table 2.

[0047]

[Table 2]

		Catalytically cracked gasoline D	Catalytically cracked light gasoline E	Catalytically cracked light gasoline F	Desulfurized catalytically cracked light gasoline G
Density (15°C) [g/cm ³]		0.7411	0.6704	0.6703	0.6700
Vapor pressure (37.8 °C) [kPa]		58.0	96.0	95.0	94.5
Hydrocarbon composition [vol%]					
50	Saturated component	45.7	47.1	46.8	47.1
	Olefin component	32.8	51.1	51.3	51.0
	Aromatic component	21.5	1.8	1.9	1.9
RON		92.0	93.9	93.9	93.9

EP 1 686 166 A1

(continued)

Hydrocarbon composition [vol%]					
Diene value [g/100g]		1.6	1.6	0.1	<0.1
Sulfur content [mass ppm]		73	21	14	0.2
Sulfur compounds content [by a sulfur, mass ppm]					
	Thiophene	4.9	7.2	6.9	0.0
	2-methylthiophene	3.8	1.4	1.6	0.2
	3-methylthiophene	4.3	1.5	1.6	0.0
	Thiophene with two or more Cs substituted	17.5	0.0	0.0	0.0
	Benzothiophenes	24.9	0.0	0.0	0.0
	C1-thiol	0.1	0.1	0.0	0.0
	C2-thiol	3.5	5.2	0.0	0.0
	C3-thiol	2.0	2.8	0.0	0.0
	C4-thiol	0.7	0.5	0.0	0.0
	C5 or more-thiol	7.3	0.0	0.3	0.0
	Sulfides	3.2	0.5	0.3	0.0
	Disulfides	0.0	0.0	0.0	0.0
Distillation properties [°C]					
	Initial boiling point	38.0	32.5	32.5	32.5
	5 vol% distillation temp	50.0	39.5	39.0	39.0
	10 vol% distillation temp	55.0	41.0	40.5	41.0
	50 vol% distillation temp	97.5	50.0	50.0	49.5
	90 vol% distillation temp	174.0	76.0	76.0	76.0
	95 vol% distillation temp	186.5	86.5	86.0	86.5
	End point	204.0	121.0	121.5	120.5

[0048] Catalytically cracked light gasoline E had a diene value of 1.6 g/100 g, whereas the diene value of catalytically cracked light gasoline F was 0.1 g/100 g, confirming sufficient removal of dienes. Catalytically cracked light gasoline F containing 14 mass ppm of sulfur was desulfurized by the treatment with the desulfurization agent and desulfurized catalytically cracked light gasoline G with a sulfur content of 0.2 mass ppm was obtained. The resulting desulfurized catalytically cracked light gasoline G contained 0.2 mass ppm of 2-methylthiophene, but did not contain thiophene and 3-methylthiophene.

Preparation of gasoline base material 3

[0049] The catalytically cracked gasoline D was subjected to a sweetening treatment to obtain a catalytically cracked

gasoline H. The catalytically cracked gasoline H was subjected to a fractional distillation into a light fraction and heavy fraction to obtain a catalytically cracked light gasoline I. The catalytically cracked light gasoline I was subjected to a diene-reducing treatment in the same manner as in the preparation of gasoline base material 2 to obtain a catalytically cracked light gasoline J. The catalytically cracked light gasoline J was subjected to a desulfurization treatment in the same manner as in the preparation of gasoline base material 1 using the copper-zinc complex oxide prepared in the preparation of gasoline base material 1 to obtain a desulfurized catalytically cracked light gasoline K. Properties of the catalytically cracked gasoline H, catalytically cracked light gasoline I, catalytically cracked light gasoline J from which dienes were removed, and desulfurized catalytically cracked light gasoline K are shown in Table 3.

[0050]

[Table 3]

		Catalytically cracked gasoline H	Catalytically cracked light gasoline I	Catalytically cracked light gasoline J	Desulfurized catalytically cracked light gasoline K
Density (15°C) [g/cm ³]		0.7411	0.6704	0.6704	0.6704
Vapor pressure (37.8 °C) [kPa]		58.0	96.0	96.5	96.0
Hydrocarbon composition [vol%]					
	Saturated component	45.7	47.0	47.1	46.9
	Olefin component	32.8	51.2	50.9	51.1
	Aromatic component	21.5	1.8	2.0	2.0
RON		92.0	93.9	93.9	93.9
Diene value [g/100g]		1.6	1.6	0.1	<0.1
Sulfur content [mass ppm]		73	11	11	0.2
Sulfur compounds content #					
	Thiophene	4.9	7.8	7.5	0.0
	2-methylthiophene	3.8	1.4	1.5	0.2
	3-methylthiophene	4.3	1.5	1.5	0.0
	Thiophene with two or more Cs substituted	17.5	0.0	0.0	0.0
	Benzothiophenes	24.9	0.0	0.0	0.0
	C1-thiol	0.0	0.0	0.0	0.0
	C2-thiol	0.0	0.0	0.0	0.0
	C3-thiol	0.0	0.0	0.0	0.0
	C4-thiol	0.0	0.0	0.0	0.0
	C5 or more-thiol	0.0	0.0	0.0	0.0
	Sulfides	3.2	0.5	0.2	0.0
	Disulfides	13.7	0.0	0.0	0.0

(continued)

Distillation properties [°C]					
5 10 15 20	Initial boiling point	38.0	32.5	32.5	32.0
	5 vol% distillation temp	50.0	39.5	39.5	39.0
	10 vol% distillation temp	55.0	41.0	41.0	41.0
	50 vol% distillation temp	97.5	50.0	50.0	49.5
	90 vol% distillation temp	174.0	76.5	76.0	75.5
	95 vol% distillation temp	186.5	86.0	86.0	86.5
	End point	204.0	121.0	121.5	120.0
#: Sulfur compounds content is indicated by the sulfur content (mass ppm).					

[0051] Light thiols contained in the catalytically cracked gasoline D were converted into disulfides with higher molecular weight by the sweetening treatment. Catalytically cracked light gasoline I was found to have a diene value of 1.6 g/100 g, whereas the diene value of catalytically cracked light gasoline J was 0.1 g/100 g, confirming sufficient removal of dienes. Catalytically cracked light gasoline J containing 11 mass ppm of sulfur was desulfurized by the treatment with the desulfurization agent, and desulfurized catalytically cracked light gasoline K with a sulfur content of 0.2 mass ppm was obtained. The resulting desulfurized catalytically cracked light gasoline K contained 0.2 mass ppm of 2-methylthiophene, but did not contain thiophene and 3-methylthiophene. Because thiols are converted into disulfides by sweetening before fractional distillation and transfer to a heavy fraction, the sulfur content in the catalytically cracked light gasoline after sweetening is reduced to 11 mass ppm from 21 mass ppm of the catalytically cracked light gasoline which was not treated by sweetening. The sweetening treatment thus reduced a load of sorption agent and increases its life.

Preparation of gasoline base material 4

[0052] The catalytically cracked gasoline A and catalytically cracked light gasoline E were subjected to a desulfurization treatment under the same conditions as in the preparation of gasoline base material 1 using the copper-zinc complex oxide prepared in the preparation of gasoline base material 1 to obtain a desulfurized catalytically cracked gasoline L and desulfurized catalytically cracked light gasoline M, respectively. Properties of the desulfurized catalytically cracked gasoline L and desulfurized catalytically cracked light gasoline M are shown in Table 4.

[0053]

[Table 4]

		Desulfurized catalytically cracked gasoline L	Desulfurized catalytically cracked light gasoline M
45	Density (15°C) [g/cm ³]	0.7325	0.6704
	Vapor pressure (37.8 °C) [kPa]	72.0	96.0
	Hydrocarbon composition [vol%]		
50	Saturated component	53.8	50.5
	Olefin component	23.1	48.0
	Aromatic component	23.1	1.5
55	RON	91.3	93.8
	Diene value [g/100g]	0.6	1.6

(continued)

Hydrocarbon composition [vol%]			
Sulfur content [mass ppm]		3.6	11
Sulfur compounds content [by a sulfur, mass ppm]			
	Thiophenes	3.6	10.7
	Thiophene	0.6	7.8
	2-methylthiophene	0.5	1.4
	3-methylthiophene	0.5	1.5
	Thiophene with two or more Cs substituted	2.0	0.0
	Benzothiophenes	0.0	0.0
	Thiols	0.0	0.0
	C1-thiol	0.0	0.0
	C2-thiol	0.0	0.0
	C3-thiol	0.0	0.0
	C4-thiol	0.0	0.0
	C5 or more-thiol	0.0	0.0
	Sulfides	0.0	0.0
	Disulfides	0.0	0.0
Distillation properties [°C]			
	Initial boiling point	31.5	32.5
	5 vol% distillation temp	40.0	39.0
	10 vol% distillation temp	45.0	41.5
	50 vol% distillation temp	89.5	50.0
	90 vol% distillation temp	166.0	76.0
	95 vol% distillation temp	178.0	86.5
	End point	207.5	122.0

[0054] It can be seen that the desulfurized catalytically cracked gasoline L and desulfurized catalytically cracked light gasoline M contain 3.6 mass ppm of sulfur and 11 mass ppm of sulfur respectively, indicating that removal particularly of thiophenes is difficult by the sorption treatment if dienes are not removed.

Preparation of gasoline base material 5

[0055] As gasoline base materials available by known technologies other than catalytic cracking, desulfurized straight run naphtha N, catalytically reformed middle oil O, catalytically reformed heavy oil P, alkylate gasoline Q, and ETBE stock R can be given. Their properties are shown in Table 5. The catalytically reformed middle oil O was obtained by separating fractions containing a large amount of toluene from catalytically reformed gasoline by distillation. The catalytically reformed heavy oil P was obtained by separating aromatics having 9-10 carbon atoms from catalytically reformed gasoline by distillation.

[0056]

EP 1 686 166 A1

[Table 5]

		Desulfurized straight run naphtha N	Catalytically reformed middle oil O	Catalytically reformed heavy oil P	Alkylate gasoline Q	ETBE R
	Density (15°C) [g/cm ³]	0.6645	0.8700	0.8798	0.7009	0.7454
	Vapor pressure (37.8 °C) [kPa]	83.0	9.0	5.0	43.5	49.5
	Hydrocarbon composition [vol%]					
	Saturated component	98.3	2.0	0.0	100.0	100.0
	Olefin component	0.1	0.0	0.0	0.0	0.0
	Aromatic component	1.6	98.0	100.0	0.0	0.0
	RON	68.0	108.1	114.0	96.5	112.0
	Sulfur content [mass ppm]	<0.1	<0.1	<0.1	<0.1	<0.1
	Thiophene compounds content #	<0.1	<0.1	<0.1	<0.1	<0.1
	Distillation properties [°C]					
	Initial boiling point	32.0	99.0	160.5	35.0	66.5
	10 vol% distillation temp	46.5	106.0	163.0	81.5	70.2
	50 vol% distillation temp	60.5	108.5	165.0	105.0	72.5
	90 vol% distillation temp	76.5	111.0	172.5	122.0	73.6
	95 vol% distillation temp	83.0	112.5	180.5	160.5	75.0
	End point	99.0	127.0	208.0	198.0	89.2
#: Sulfur compounds content is indicated by the sulfur content (mass ppm).						

EXAMPLE 1

[0057] 10.0 vol% of desulfurized straight run naphtha N, 5.0 vol% of catalytically reformed middle oil O, 5.0 vol% of catalytically reformed heavy oil P, 5.0 vol% of alkylate gasoline Q, and 75.0 vol% of desulfurized catalytically cracked gasoline C obtained in the preparation of gasoline base material 1 were blended to obtain unleaded gasoline composition S. As additives, 2 mg/L of a coloring agent ("CL-53" manufactured by Shirado Chemical Co., Ltd.), 20 mg/L of an antioxidant ("Sumilizer 4ML" manufactured by Sumitomo Chemical Co., Ltd.), and 100 mg/L of a detergent-dispersants ("Keropur AP-95" manufactured by BASF) were added. These additives were also added exactly in the same manner in the preparation of unleaded gasoline compositions in the following Examples and Comparative Examples. The properties of the resulting unleaded gasoline composition S are shown in Table 6.

EXAMPLE 2

[0058] 3.5 vol% of desulfurized straight run naphtha N, 19.0 vol% of catalytically reformed middle oil O, 15.0 vol% of catalytically reformed heavy oil P, 23.0 vol% of alkylate gasoline Q, and 39.5 vol% of desulfurized catalytically cracked light gasoline K obtained in the preparation of gasoline base material 3 were blended to obtain unleaded gasoline composition T. The properties of the resulting unleaded gasoline composition T are shown in Table 6.

EXAMPLE 3

[0059] 6.0 vol% of desulfurized straight run naphtha N, 8.0 vol% of catalytically reformed middle oil O, 5.0 vol% of catalytically reformed heavy oil P, 8.0 vol% of alkylate gasoline Q, 6.0 vol% of ETBE, and 67.0 vol% of desulfurized catalytically cracked gasoline C obtained in the preparation of gasoline base material 1 were blended to obtain unleaded gasoline composition U. The properties of the resulting unleaded gasoline composition U are shown in Table 6.

EXAMPLE 4

[0060] 6.0 vol% of desulfurized straight run naphtha N, 9.0 vol% of catalytically reformed middle oil O, 8.0 vol% of catalytically reformed heavy oil P, 10.0 vol% of alkylate gasoline Q, 57.0 vol% of desulfurized catalytically cracked gasoline C obtained in the preparation of gasoline base material 1, and 10.0 vol% of desulfurized catalytically cracked light gasoline K obtained in the preparation of gasoline base material 3 were blended to obtain unleaded gasoline composition V. The properties of the resulting unleaded gasoline composition V are shown in Table 6.

[0061]

[Table 6]

		Unleaded gasoline composition							
		S	T	U	V	W	X	Y	Z
		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Example 5	Comparative Example 3
Density (15°C) [g/cm ³]		0.7379	0.7451	0.7428	0.7446	0.7378	0.7450	0.7392	0.7384
Vapor pressure (37.8°C) [kPa]		63.0	54.5	60.0	59.0	66.0	54.0	52.5	52.0
Hydrocarbon composition [vol%]									
	Saturated component	55.1	46.8	51.3	55.9	55.3	46.8	49.5	48.7
	Olefin component	17.4	19.0	18.3	15.6	17.4	19.1	22.3	23.0
	Aromatic component	27.5	34.3	30.4	28.5	27.3	34.2	28.2	28.3
RON		91.8	99.3	94.0	94.0	91.8	99.3	91.5	91.7
Sulfur content [mass ppm]		0.1	0.1	0.1	0.1	12.0	3.9	0.5	14.7
Thiophene compounds content #		0.1	0.1	0.1	0.1	2.9	3.9	0.5	6.9
Thiophene #		0.0	0.0	0.0	0.0	1.2	2.8	0.0	0.6
2-methylthiophene #		0.1	0.1	0.1	0.1	0.4	0.5	0.1	0.9
Thiol compounds content #		0.0	0.0	0.0	0.0	8.0	0.0	0.0	0.0

55 50 45 40 35 30 25 20 15 10 5

(continued)

Distillation properties [°C]									
	Initial boiling point	33.0	32.0	32.5	34.5	33.0	32.0	32.5	32.0
	5 vol% distillation temp	46.0	41.0	43.5	47.0	45.0	41.0	41.5	41.5
	10 vol% distillation temp	49.5	44.0	48.0	52.0	49.0	44.5	44.0	44.5
	50 vol% distillation temp	95.5	94.5	99.0	97.5	94.5	94.5	98.5	99.0
	90 vol% distillation temp	166.0	164.5	165.5	165.0	166.0	164.0	170.0	169.5
	95 vol% distillation temp	175.5	169.0	173.0	174.0	176.0	169.0	180.5	180.5
	End point	192.0	185.0	188.5	189.0	193.0	187.0	196.5	195.5
#: Sulfur compounds content is indicated by the sulfur content (mass ppm).									

COMPARATIVE EXAMPLE 1

[0062] An unleaded gasoline composition W was prepared in the same manner as the preparation of the unleaded gasoline composition S in Example 1, except for using the catalytically cracked gasoline A instead of desulfurized catalytically cracked gasoline C. The properties of the resulting unleaded gasoline composition W are shown in Table 6.

COMPARATIVE EXAMPLE 2

[0063] An unleaded gasoline composition X was prepared in the same manner as the preparation of the unleaded gasoline composition T in Example 2, except for using the catalytically cracked light gasoline I described in the preparation of gasoline base material 3 instead of the desulfurized catalytically cracked light gasoline K described in the preparation of gasoline base material 3. The properties of the resulting unleaded gasoline composition X are shown in Table 6.

[0064] It can be seen from Table 6 that as compared with the unleaded gasoline composition W prepared in conventional technology, the unleaded gasoline composition S of the present invention has a reduced sulfur content of 1 mass ppm or less, with other properties being almost the same as those of the unleaded gasoline composition W. It can also be seen from Table 6 that the unleaded gasoline composition T of the present invention has a reduced sulfur content of 1 mass ppm or less, with other properties being almost the same as those of the unleaded gasoline composition X corresponding to the unleaded gasoline composition T. The sulfur content of the unleaded gasoline compositions U and V of the present invention was also successfully reduced to 1 mass ppm or less.

Preparation of gasoline base material 6

[0065] A catalytically cracked gasoline AA was prepared in the same manner as in the preparation of gasoline base material 1 using different lot of Middle East crude oil from the lot of Middle East crude oil used in the preparation of gasoline base material 1 and subjected to a sweetening treatment, followed by fractional distillation into a light fraction and a heavy fraction. The heavy fraction was obtained as a catalytically cracked heavy gasoline BB. The catalytically cracked heavy gasoline BB was subjected to a diene-reducing treatment using a catalyst supported with cobalt, molybdenum, and phosphorus carried on alumina (Co: 2.4 mass%, Mo: 9.4 mass%, P: 2.0 mass%) under the conditions of the reaction temperature of 220°C, reaction pressure of 1.0 MPa, LHSV of 4.0 hr⁻¹, and H₂/Oil ratio of 307 NL/L to obtain a catalytically cracked heavy gasoline CC having a diene value of 0.6 to 0.1 g/100g. The diene-removed catalytically cracked heavy gasoline CC was desulfurized exactly in the same manner and under the same conditions as in the preparation of gasoline base material 1, except for employing an H₂/Oil ratio of 0.18 NL/L, to obtain desulfurized catalytically cracked heavy gasoline DD with a sulfur content of 0.9 mass ppm. The properties of each gasoline (catalytically cracked gasoline AA to desulfurized catalytically cracked heavy gasoline DD) are shown in Table 7.

Preparation of gasoline base material 7

[0066] The catalytically cracked heavy gasoline BB used in the preparation of gasoline base material 6 was desulfurized, without subjecting to the diene-reducing treatment, in the same manner and under the same conditions as in the preparation of gasoline base material 1, except for employing an H₂/Oil ratio of 0.18 NL/L, to obtain desulfurized catalytically cracked heavy gasoline EE. The properties of the desulfurized catalytically cracked heavy gasoline EE are shown in Table 7.

[0067]

[Table 7]

	Catalytically cracked gasoline AA	Catalytically cracked heavy gasoline BB	Diene-removed catalytically cracked heavy gasoline CC	Desulfurized catalytically cracked heavy gasoline DD	Desulfurized catalytically cracked heavy gasoline EE
Density (15°C) [g/cm ³]	0.7250	0.7904	0.7932	0.7941	0.7920
Vapor pressure (37.8°C) [kPa]	74.0	9.0	11.0	12.0	11.0
Hydrocarbon composition [vol%]					

EP 1 686 166 A1

(continued)

		Catalytically cracked gasoline AA	Catalytically cracked heavy gasoline BB	Diene-removed catalytically cracked heavy gasoline CC	Desulfurized catalytically cracked heavy gasoline DD	Desulfurized catalytically cracked heavy gasoline EE
	Saturated component	55.6	43.7	46.7	46.9	44.0
	Olefin component	25.1	12.7	11.1	10.8	12.4
	Aromatic component	19.3	43.6	42.2	42.3	43.6
	RON	91.9	88.5	87.5	87.4	88.4
	Diene value [g/100g]	0.6	0.7	<0.1	<0.1	<0.1
	Sulfur content [mass ppm]	26.0	78.5	7.4	0.9	42
	Sulfur compounds content #					
	Thiophenes	8.4	21.8	1.8	0.9	19.6
	Benzothiophenes	1.3	26.2	0.0	0.0	21.5
	Thiols	14.8	0.2	5.6	0.0	0.0
	Sulfides	1.3	2.6	0.0	0.0	0.6
	Disulfides	0.0	27.0	0.0	0.0	0.3
	Distillation properties [°C]					
	Initial boiling point	31.5	87.0	91.0	89.5	87.5
	5 vol% distillation temp	40.0	101.0	103.5	104.5	100.5
	10 vol% distillation temp	45.5	106.5	108.5	109.5	105.5
	50 vol% distillation temp	89.0	136.5	139.0	139.5	135.5
	90 vol% distillation temp	164.5	186.5	186.5	186.0	186.0
	95 vol% distillation temp	177.0	195.5	194.5	195.0	194.5
	End point	200.0	209.0	208.5	209.0	206.0
#: Sulfur compounds content is indicated by the sulfur content (mass ppm).						

EXAMPLE 5

[0068] 10.0 vol% of desulfurized straight run naphtha N, 7.0 vol% of catalytically reformed middle oil O, 5.0 vol% of catalytically reformed heavy oil P, 6.0 vol% of alkylate gasoline Q, 37.0 vol% of desulfurized catalytically cracked light gasoline K obtained in the preparation of gasoline base material 3, and 35.0 vol% of desulfurized catalytically cracked heavy gasoline DD obtained in the preparation of gasoline base material 6 were blended to obtain unleaded gasoline composition Y. The properties of the unleaded gasoline composition Y are shown in Table 6.

Comparative Example 3

[0069] An unleaded gasoline composition Z was prepared in the same manner as in Example 5, except for using the

desulfurized catalytically cracked heavy gasoline EE obtained in the preparation of gasoline base material 7 instead of the desulfurized catalytically cracked heavy gasoline DD. The properties of the resulting unleaded gasoline composition Z are shown in Table 6.

[0070] It can be seen from comparison of the properties of the desulfurized catalytically cracked heavy gasoline DD of the preparation gasoline base material 6 with the properties of the desulfurized catalytically cracked heavy gasoline EE of the preparation gasoline base material 7 in Table 7 that it is very difficult to reduce the sulfur content to 1 mass ppm or less in the gasoline, though the gasoline is desulfurized using a desulfurization agent having a sorption function as holding a high diene value and a high sulfur content. Therefore, as shown in Table 6 as unleaded gasoline composition Y, an unleaded gasoline composition having a sulfur content of 1 mass ppm or less and exhibiting sufficient driving performance can be easily obtained by blending the desulfurized catalytically cracked heavy gasoline DD, which was obtained by desulfurization using a desulfurization agent having a sorption function after diene-reducing treatment, with another gasoline base materials with a low sulfur content.

Reference Example

[0071] 5 cm³ of the same copper-zinc-aluminum complex oxide (Cu: 35 mass%, Zn: 35 mass%, Al: 5 mass%) as described in the preparation of gasoline base material 1 was loaded in a reactor tube and subjected to a reduction treatment by flowing hydrogen gas at 5 cm³/min for 16 hours. Then, toluene containing 263 mass ppm of thiophene (100 mass ppm as S) was flowed to the reactor tube under the conditions of a reaction temperature of 100°C, atmospheric pressure, LHSV of 2.0 hr⁻¹, and H₂/Oil ratio of 0.18 NL/L to obtain a product shown in Table 8.

[0072]

[Table 8]

		Product selection rate [mol% on the basis of raw thiophene]
Hydrogen sulfide		<0.1
Hydrocarbon		
	1-Butene	76
	cis-2-Butene	14
	trans-2-Butene	7
	n-Butane	3
Thiophene		<0.1

[0073] It can be seen from Table 8 that sulfur was removed from thiophene in the raw oil to produce hydrocarbons originating from hydrocarbon residues other than the sulfur atom in thiophene by the treatment using a copper-zinc-aluminum complex oxide in the presence of hydrogen, but no hydrogen sulfide was produced. Thus, it is clear that the copper-zinc-aluminum complex oxide functioned as the porous desulfurization agent with a sulfur sorption function of the present invention.

INDUSTRIAL APPLICABILITY

[0074] According to the present invention an unleaded gasoline composition with a sulfur content of 1 mass ppm or less can be produced by mixing a desulfurized cracked naphtha fraction, which is obtained from cracked gasoline by removing dienes and desulfurizing using a porous desulfurization agent having a sulfur sorption function in the presence of a small amount of hydrogen, while leaving olefins unchanged to avoid octane number reduction accompanying the desulfurization, and another gasoline base material with a sulfur content of 10 mass ppm or less. Therefore, it is possible to reduce only the sulfur content to 1 mass ppm or less, while changing almost no other properties in conventional unleaded gasoline compositions. The unleaded gasoline composition of the present invention is useful as a vehicle fuel exhibiting high driving performance, while imposing a minimal load to environment.

Claims

1. A method for producing the unleaded gasoline composition having a sulfur content of 1 mass ppm or less and a research octane number of 89.0 or more, comprising a desulfurization step of subjecting a cracked naphtha fraction

having a 5 vol% distillation temperature of 25°C or more, a 95 vol% distillation temperature of 210°C or less, an olefin content of 5 mass% or more, and a diene value of 0.3 g/100 g or less to a desulfurization treatment, and a blending step of mixing the resulting desulfurized cracked naphtha fraction with another gasoline base materials.

- 5 **2.** The method for producing the unleaded gasoline composition according to claim 1, further comprising a diene-reducing step of reducing the diene content of the raw cracked naphtha fraction by causing the cracked naphtha fraction to come into contact with a diene-reducing catalyst in advance.
- 10 **3.** The method for producing the unleaded gasoline composition according to claim 2, wherein the diene-reducing catalyst comprises at least one metal selected from group 8 elements in the periodic table.
- 4.** The method for producing the unleaded gasoline composition according to claim 3, wherein at least one metal contained in the diene-reducing catalyst is nickel or cobalt.
- 15 **5.** The method for producing the unleaded gasoline composition according to any of claims 1-4, wherein the desulfurization treatment comprises causing the cracked naphtha fraction to come in contact with a porous desulfurization agent having a sulfur sorption function in the presence of hydrogen under hydrogen partial pressure of 1 MPa
- 20 **6.** The method for producing the unleaded gasoline composition according to claim 5, wherein the porous desulfurization agent comprises at least one metal selected from copper, zinc, nickel, and iron.
- 7.** The method for producing the unleaded gasoline composition according to any of claims 1-6, wherein the blending step comprises mixing 10-90 vol% of the desulfurized cracked naphtha fraction with 90-10 vol% of another gasoline base materials.
- 25 **8.** The method for producing the unleaded gasoline composition according to any of claims 1-7, wherein the cracked naphtha fraction is a light cracked naphtha fraction having a 5 vol% distillation temperature of 25-43°C, a 95 vol% distillation temperature of 55-100°C, an olefin content of 5 mass% or more, and a diene value of 0.3 g/100 g or less.
- 30 **9.** The method for producing the unleaded gasoline composition according to claim 8, wherein the light cracked naphtha fraction is obtained by subjecting the cracked naphtha fraction to a diene-reducing treatment, followed by fractional distillation, or fractionating the cracked naphtha fraction, followed by a diene-reducing treatment, or simultaneous fractional distillation and diene-reducing treatment of the cracked naphtha fraction.
- 35 **10.** The method for producing the unleaded gasoline composition according to claim 9, further comprising a pretreatment step of subjecting the raw fraction of the cracked naphtha fraction prior to or simultaneously with the fractional distillation for obtaining a light cracked naphtha fraction, or the raw fraction of the cracked naphtha fraction subjected to a diene-reducing treatment to increase the molecular weight of sulfur compounds therein.
- 40 **11.** The method for producing the unleaded gasoline composition according to any of claims 8-10, wherein the blending step comprises mixing 10-60 vol% of the light desulfurized cracked naphtha fraction with 90-40 vol% of another gasoline base materials, and the unleaded gasoline composition has a research octane number of 93.0 or more.
- 45 **12.** An unleaded gasoline composition having a research octane number of 89.0 or more, a 50 vol% distillation temperature of 105°C or less, an olefin content of 10 vol% or more, a total sulfur content of 1 mass ppm or less, and a proportion of thiophene compounds to the total sulfur compounds of 50 mass% or more, as sulfur.
- 13.** The unleaded gasoline composition according to claim 12, having a research octane number of 93.0 or more.
- 50 **14.** The unleaded gasoline composition according to claim 13, having a proportion of olefins having a boiling point of 35-100 °C to the total olefins of 90.0 vol% or more.
- 15.** The unleaded gasoline composition according to claim 13, having a proportion of total amount of thiophene and 2-methylthiophene to the total sulfur compounds of 50 mass% or more, as sulfur.
- 55 **16.** The unleaded gasoline composition according to any of claims 12-15, having a thiol compounds content of 0.1 mass ppm or less, as sulfur.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/016115

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C10L1/06, 1/00, C10G29/04, 53/08, 53/10, 55/06 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C10L1/06, 1/00, C10G29/04, 53/08, 53/10, 55/06 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2001-303070 A (Idemitsu Kosan Co., Ltd.), 31 October, 2001 (31.10.01), Claims; Par. Nos. [0008] to [0013], [0026] & AU 1893101 A & EP 1243636 A1 & US 2003-23120 A & WO 2001-44412 A & JP 2001-172651 A & 2001-262161 A	1-16
A	WO 2002-31090 A1 (Nippon Oil Corp.), 18 April, 2002 (18.04.02), Claims; page 8, line 41 to page 9, line 24; tables 4, 5 & AU 9422601 A & EP 1340800 A1 & US 2003-213728 A	1-16
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 11 November, 2004 (11.11.04)		Date of mailing of the international search report 30 November, 2004 (30.11.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/016115

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-73677 A (Idemitsu Kosan Co., Ltd.), 12 March, 2003 (12.03.03), Claims; Par. Nos. [0011] to [0013], [0021] to [0025] (Family: none)	1-16
A	JP 2003-301186 A (Kabushiki Kaisha Jomo Technical Research Center), 21 October, 2003 (21.10.03), Claims; Par. Nos. [0015] to [0016], [0024] (Family: none)	1-16

Form PCT/ISA/210 (continuation of second sheet) (January 2004)