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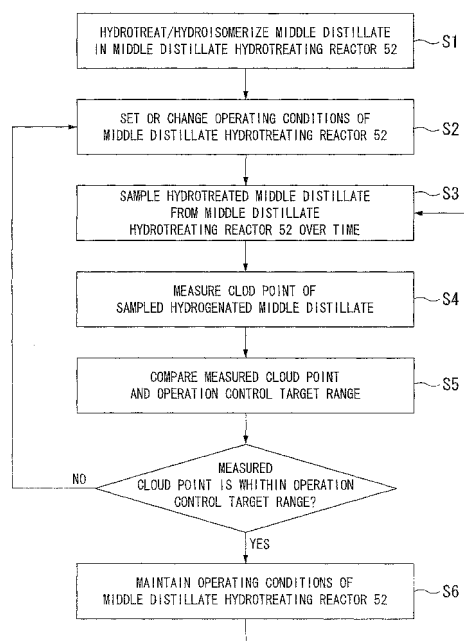
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(54) **METHOD OF OPERATING INTERMEDIATE-FRACTION HYDROFINING REACTOR AND INTERMEDIATE-FRACTION HYDROFINING REACTOR**

(57) There is provided an operation method of a middle distillate hydrotreating reactor which hydrotreats and hydroisomerizes a middle distillate including components of a boiling point range equivalent to gas oil among FT synthesis hydrocarbons synthesized by the Fisher-Tropsch synthesis reaction, the operation method comprising the steps of: bringing the middle distillate into contact with a catalyst to hydrotreat and hydroisomerize the middle distillate to produce hydrotreated middle distillate; measuring the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor; and controlling the operating conditions of the middle distillate hydrotreating reactor so that the cloud point comes to a predetermined target value.

FIG. 4



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Description

[Technical Field]

[0001] The present invention relates to an operation method of a middle distillate hydrotreating reactor, and the middle distillate hydrotreating reactor, which hydrotreat and hydroisomerize a middle distillate including a component of a boiling point range equivalent to gas oil among hydrocarbon compounds synthesized by the Fisher-Tropsch synthesis reaction. Priority is claimed on Japanese Patent Application No. 2009-020855, filed January 30, 2009, the content of which is incorporated herein by reference.

[Background Art]

[0002] As one of methods for synthesizing liquid fuels from a natural gas, a GTL (Gas To Liquids: liquid fuel synthesis) technique of reforming a natural gas to produce a synthesis gas containing a carbon monoxide gas (CO) and a hydrogen gas (H₂) as main components, synthesizing hydrocarbon compounds (hereinafter referred to as "FT synthesis hydrocarbons") using this synthesis gas as a source gas by the Fischer-Tropsch synthesis reaction (hereinafter referred to as an "FT synthesis reaction"), and further hydrotreating and fractionating the FT synthesis hydrocarbons to produce liquid fuel products, such as naphtha (raw gasoline), kerosene, gas oil (diesel fuel oil), and wax, has recently been developed.

[0003] Here, since the liquid fuel products using the aforementioned FT synthesis hydrocarbons as a feedstock have high paraffin content, and almost no sulfur component, for example, as shown in Patent Document 1, the liquid fuel products attract attention as an environmentally friendly fuel.

When the FT synthesis hydrocarbons are fractionated in a fractionator, a middle distillate including a component of a boiling point range equivalent to gas oil is taken out from a middle part of the fractionator. This middle distillate is used as a feedstock of gas oil. Additionally, a wax fraction with a large carbon number is taken out from the bottom of the fractionator. This wax fraction can be made light by hydrocracking, and can thereby be used as a feedstock of gas oil.

[0004] Here, since a large amount of normal paraffins is included in the aforementioned middle distillate of the FT synthesis hydrocarbons, the freezing point (freezing temperature) tends to become high, and there is a possibility that the cold properties of gas oil obtained from this middle distillate used as a feedstock does not satisfy demanded specifications as a product. For this reason, as for the middle distillate distilled from the fractionator, when olefins and oxygen-containing compounds such as alcohols, which are produced as by-products in an FT synthesis reaction process, are converted into saturated hydrocarbons by hydrotreating, it is necessary to perform hydroisomerization to convert at least a portion of the normal paraffins into isoparaffins having a low freezing point.

[Citation List]

[Patent Document]

[0005] [Patent Document 1] Japanese Patent Unexamined Publication No. 2004-323626

[Summary of Invention]

[Technical Problem]

[0006] If the progress of the hydroisomerization is insufficient in a middle distillate hydrotreating process which hydrotreats and hydroisomerizes the middle distillate, a lot of normal paraffins with a high freezing point remain in the obtained hydrotreated middle distillate, and the cold properties of the gas oil obtained from this middle distillate used as a feedstock are not sufficiently improved. On the other hand, in a case where the reaction conditions are selected so that hydroisomerization proceeds excessively in the middle distillate hydrotreating process, a decomposition reaction concurs to lighten the generated hydrocarbons, and there is a possibility that middle distillate may not be suitable as a feedstock of gas oil, and the yield of the gas oil as a product may decrease.

For this reason, in order to obtain gas oil (diesel fuel oil) from the FT synthesis hydrocarbons, it is necessary to properly progress the hydroisomerization in the hydrotreating process of the middle distillate.

[0007] The present invention was made in view of the aforementioned situation, and the object of the present invention is to provide an operation method of a middle distillate hydrotreating reactor, and the middle distillate hydrotreating reactor, capable of properly progressing hydroisomerization in a hydrotreating process of a middle distillate of FT synthesis hydrocarbons obtained by the FT synthesis reaction, producing a hydrotreated middle distillate with stable properties, and obtaining high-quality gas oil.

[Solution to Problem]

[0008] In order to solve the above problem and achieve such an object, the present invention suggests the following methods.

The operation method of a middle distillate hydrotreating reactor which hydrotreats and hydroisomerizes a middle distillate including components of a boiling point range equivalent to gas oil among FT synthesis hydrocarbons synthesized by the Fisher-Tropsch synthesis reaction. The operation method comprising the steps of: bringing the middle distillate into contact with a catalyst to hydrotreat and hydroisomerize the middle distillate to produce hydrotreated middle distillate; measuring the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor; and controlling the operating conditions of the middle distillate hydrotreating reactor so that the cloud point comes to a predetermined target value.

[0009] In the operation method of a middle distillate hydrotreating reactor having the above configuration, the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor, is measured, and the operating conditions of the middle distillate hydrotreating reactor are controlled so that the cloud point becomes a predetermined target value. Therefore, the cloud point of the produced hydrotreated middle distillate gets stable. In addition, the cloud point is the temperature when a component with a high freezing point (wax) precipitates as a solid in liquid hydrocarbons (middle distillate), and clouding occurs. As shown in JIS K 2269, for example, the cloud point can be measured by cooling a sample liquid at a certain rate, and measuring the liquid temperature when the clouding has occurred in the sample liquid.

Here, in a case where a large amount of normal paraffins is included in the produced hydrotreated middle distillate, the cloud point of the hydrotreated middle distillate becomes high. On the other hand, in a case where the content of normal paraffins in the hydrotreated middle distillate is small, the cloud point of the hydrotreated middle distillate becomes low. That is, it is possible to understand the degree of the hydroisomerization in the middle distillate hydrotreating reactor by measuring the cloud point of the hydrotreated middle distillate.

[0010] Accordingly, by measuring the cloud point of the hydrotreated middle distillate, and controlling the operating conditions of the middle distillate hydrotreating reactor based on this measurement value, it is possible to properly progress the hydroisomerization in the reactor, to produce a hydrotreated middle distillate with stable properties, and to obtain high-quality gas oil.

In addition, in a case where gas oil as diesel fuel oil is used under cold conditions, the normal paraffins precipitates as a wax component, and thus, plugging may occur in a filter installed in a fuel-oil supply system to a diesel engine. Then, for the purpose of preventing such a problem, generally gas oil products are managed so as to have a cloud point lower than or equal to a certain value. However, in a reactor of a producing process of a middle distillate used as a feedstock of the gas oil, the cloud point has not been used as an index of operation management conventionally.

[0011] In the operation method of a middle distillate hydrotreating reactor of the present invention, in the step of measuring the cloud point, the cloud point may be measured while cooling a obtained sample of the hydrotreated middle distillate at a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less.

In this case, it is possible to measure the cloud point in a short time by measuring the cloud point while cooling the sample at a cooling rate of 5.0 °C/min or more. As a result, the measurement result of the cloud point can be reflected on the control of the middle distillate hydrotreating reactor, without being accompanied by a large time lag after the taking of the sample of the hydrotreated middle distillate. Additionally, by measuring the cloud point while cooling the sample at a cooling rate of 15.0 °C/min or less, it is possible to accurately measure the cloud point, and it is possible to appropriately control the middle distillate hydrotreating reactor.

[0012] Additionally, in the operation method of a middle distillate hydrotreating reactor of the present invention, in the step of measuring the cloud point, the cloud point may be measured while cooling the obtained sample at the cooling rate controlled by an electronic cooling unit using a Peltier device.

In this case, by cooling the hydrotreated middle distillate with the electronic cooling unit using the Peltier device, it is possible to accurately and easily perform the temperature control of the hydrotreated middle distillate, and it is possible to accurately measure the cloud point.

[0013] Moreover, in the operation method of a middle distillate hydrotreating reactor of the present invention, in the step of controlling the operating conditions of the middle distillate hydrotreating reactor, at least one of hydrogen partial pressure, reaction temperature, and throughput of middle distillate per unit time may be controlled.

In this case, it is possible to adjust the degree of the hydroisomerization by controlling at least one of hydrogen partial pressure, reaction temperature, and throughput of middle distillate per unit time, which are the operation conditions of the middle distillate hydrotreating reactor. In addition, the throughput of middle distillate per unit time can be expressed by liquid hourly space velocity (LHSV(h⁻¹)) as the amount of oil through the middle distillate hydrotreating reactor.

For example, if the cloud point exceeds the upper limit of an operation control target range, the hydroisomerization is promoted and the cloud point of the hydrotreated middle distillate can be lowered, by setting the conditions that the hydrogen partial pressure is raised, and/or the reaction temperature is raised, and/or the throughput of middle distillate

per unit time (LHSV) is reduced. Additionally, if the cloud point falls below the lower limit of the operation control target range, the progress of the hydroisomerization is suppressed and the cloud point of the hydrotreated middle distillate can be elevated, by setting the conditions that the hydrogen partial pressure is reduced, and/or the reaction temperature is lowered, and/or the throughput of middle distillate per unit time (LHSV) is increased.

[0014] The middle distillate hydrotreating reactor of the present invention is a middle distillate hydrotreating reactor which hydrotreats and hydroisomerizes a middle distillate including a component of a boiling point range equivalent to gas oil among FT synthesis hydrocarbons synthesized by the Fisher-Tropsch synthesis reaction. The reactor includes: a sampling unit which takes a sample of the produced hydrotreated middle distillate; and a cloud point measuring unit which measures the cloud point of the obtained sample.

[0015] According to the middle distillate hydrotreating reactor having this configuration, the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor is rapidly measured. Then, by controlling the operating conditions based on the result, it is possible to appropriately adjust the degree of the hydroisomerization, and to stabilize the properties of the produced hydrotreated middle distillate. This makes it possible to improve the quality of the gas oil produced from the middle distillate.

[0016] In the middle distillate hydrotreating reactor of the present invention, the sampling unit may be connected to the cloud point measuring unit by piping so as to automatically take the sample and transfer the sample to the cloud point measuring unit, and the cloud point measuring unit may automatically measure the cloud point of the transferred sample.

[0017] Additionally, in the middle distillate hydrotreating reactor of the present invention, the cloud point measuring unit may include a cooler capable of cooling the obtained sample at a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less.

In this case, as it is possible to cool the sample at the aforementioned cooling rate, the cloud point can be measured rapidly and accurately.

[0018] Moreover, in the middle distillate hydrotreating reactor of the present invention, the cooler capable of cooling the sample at a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less provided at the cloud point measuring unit may be an electronic cooling unit using a Peltier device.

In this case, it is possible to accurately and easily perform the temperature control of the sample, and the cloud point can be measured more accurately.

[Advantageous Effects of Invention]

[0019] According to the present invention, it is possible to provide an operation method of a middle distillate hydrotreating reactor, and the middle distillate hydrotreating reactor, capable of properly controlling the progress of hydroisomerization in a hydrotreating process of a middle distillate of FT synthesis hydrocarbons obtained by the FT synthesis reaction, producing a hydrotreated middle distillate with stable properties, and obtaining high-quality gas oil (diesel fuel oil).

[Brief Description of Drawings]

[0020]

[FIG 1] FIG. 1 is a schematic diagram showing the overall configuration of a liquid-fuel synthesizing system including a middle distillate hydrotreating reactor according to an embodiment of the present invention.

[FIG 2] FIG. 2 is a detailed explanatory view of the surroundings of the middle distillate hydrotreating reactor according to the embodiment of the present invention.

[FIG 3] FIG. 3 is a schematic configuration diagram of a cloud point measuring unit shown in FIG 2.

[FIG. 4] FIG. 4 is a flow chart showing an operation method of the middle distillate hydrotreating reactor according to the embodiment of the present invention.

[FIG. 5] FIG. 5 is a graph showing results of confirmatory experiments.

[Description of Embodiments]

[0021] A preferred embodiment (hereinafter referred to as the "present embodiment") of the present invention will be described below with reference to the accompanying drawings.

First, with reference to FIG 1, the overall configuration and process of a liquid-fuel synthesizing system (hydrocarbon synthesis reaction system) where an operation method of a middle distillate hydrotreating reactor that is the present embodiment is used will be described.

[0022] As shown in FIG 1, the liquid-fuel synthesizing system 1 (hydrocarbon synthesis reaction system) according to the present embodiment is a plant facility which carries out the GTL process which converts a hydrocarbon feedstock,

such as a natural gas, into liquid fuels. This liquid-fuel synthesizing system 1 includes a synthesis gas production unit 3, an FT synthesis unit 5, and an upgrading unit 7.

The synthesis gas production unit 3 reforms a natural gas, which is a hydrocarbon feedstock, to produce a synthesis gas including a carbon monoxide gas and a hydrogen gas.

5 The FT synthesis unit 5 produces liquid hydrocarbons by the FT synthesis reaction from the synthesis gas produced in the synthesis gas production unit 3.

The upgrading unit 7 hydrotreats and fractionates the liquid hydrocarbons produced by the FT synthesis reaction to produce liquid fuels (naphtha, kerosene, gas oil, wax, etc.). Hereinafter, components of these respective units will be described.

10 **[0023]** The synthesis gas production unit 3 mainly includes a desulfurization reactor 10, a reformer 12, a waste heat boiler 14, vapor-liquid separators 16 and 18, a CO₂ removal unit 20, and a hydrogen separator 26.

The desulfurization reactor 10 is composed of a hydrodesulfurizer, etc., and removes sulfur components from a natural gas that is a feedstock.

15 The reformer 12 reforms the natural gas supplied from the desulfurization reactor 10, to produce a synthesis gas including a carbon monoxide gas (CO) and a hydrogen gas (H₂) as main components.

The waste heat boiler 14 recovers waste heat of the synthesis gas produced in the reformer 12, to produce a high-pressure steam.

The vapor-liquid separator 16 separates the water heated by the heat exchange with the synthesis gas in the waste heat boiler 14 into gas (a high-pressure steam) and liquid.

20 The vapor-liquid separator 18 removes condensed components from the synthesis gas cooled down in the waste heat boiler 14, and supplies gas components to the CO₂ removal unit 20.

The CO₂ removal unit 20 has an absorption tower 22 which removes carbon dioxide gas by using an absorbent from the synthesis gas supplied from the vapor-liquid separator 18, and a regeneration tower 24 which diffuses the carbon dioxide gas from the absorbent including the carbon dioxide gas to regenerate the absorbent.

25 The hydrogen separator 26 separates a portion of the hydrogen gas included in the synthesis gas, the carbon dioxide gas in which has been separated by the CO₂ removal unit 20.

It is to be noted herein that the above CO₂ removal unit 20 is not necessarily provided depending on the circumstances.

30 **[0024]** The FT synthesis unit 5 mainly includes, for example, a bubble column reactor (a bubble column type hydrocarbon synthesis reactor) 30, a vapor-liquid separator 34, a separator 36, a vapor-liquid separator 38, and a first fractionator 40.

The bubble column reactor 30, which is an example of a reactor which synthesizes liquid hydrocarbons from a synthesis gas, functions as an FT synthesis reactor which synthesizes liquid hydrocarbons from the synthesis gas by the FT synthesis reaction. The bubble column reactor 30 is composed of, for example, a bubble column type slurry bed reactor in which a slurry having solid catalyst particles suspended in liquid hydrocarbons (product of the FT synthesis reaction) is contained inside a column type vessel. The bubble column reactor 30 makes the carbon monoxide gas and hydrogen gas in the synthesis gas produced in the above synthesis gas production unit 3 react with each other to synthesize liquid hydrocarbons.

35 The vapor-liquid separator 34 separates the water circulated and heated through a heat transfer pipe 32 disposed in the bubble column reactor 30 into a steam (a medium-pressure steam) and a liquid.

40 The separator 36 separates the catalyst particles and liquid hydrocarbons in the slurry contained inside the bubble column reactor 30.

The vapor-liquid separator 38 is connected to the top of the bubble column reactor 30 to cool down the unreacted synthesis gas discharged from the bubble column reactor 30 and a product which is gaseous under the conditions of the bubble column reactor 30, and to separate a condensed liquid product from a gas component.

45 The first fractionator 40 fractionates the FT synthesis reaction product including the liquid hydrocarbons, which is supplied via the separator 36 and the vapor-liquid separator 38 from the bubble column reactor 30 as main components, into individual fractions.

50 **[0025]** The upgrading unit 7 includes, for example, a wax fraction hydrocracking reactor 50, a middle distillate hydrotreating reactor 52 according to the present embodiment, a naphtha fraction hydrotreating reactor 54, vapor-liquid separators 56, 58, and 60, a second fractionator 70, and a naphtha stabilizer 72.

The wax fraction hydrocracking reactor 50 is connected to the bottom of the first fractionator 40, and has the vapor-liquid separator 56 provided at the downstream thereof.

The middle distillate hydrotreating reactor 52 is connected to a middle part of the first fractionator 40, and has the vapor-liquid separator 58 provided at the downstream thereof.

55 The naphtha fraction hydrotreating reactor 54 is connected to top of the first fractionator 40, and has the vapor-liquid separator 60 provided at the downstream thereof.

The second fractionator 70 fractionates the liquid hydrocarbons supplied from the vapor-liquid separators 56 and 58.

The naphtha stabilizer 72 rectifies liquid hydrocarbons of a naphtha fraction supplied from the vapor-liquid separator 60

and the second fractionator 70, to discharge butane and components lighter than butane as flare gas, and to separate and recover hydrocarbon components having a carbon number of five or more as a naphtha product.

[0026] Next, a process (GTL process) of synthesizing liquid fuels from a natural gas by the liquid-fuel synthesizing system 1 configured as above will be described.

[0027] A natural gas (whose main component is CH_4) as a hydrocarbon feedstock is supplied to the liquid-fuel synthesizing system 1 from an external natural gas supply source (not shown), such as a natural gas field or a natural gas plant. The above synthesis gas production unit 3 reforms this natural gas to produce a synthesis gas (mixed gas including a carbon monoxide gas and a hydrogen gas as main components).

[0028] First, the above natural gas is supplied to the desulfurization reactor 10 along with the hydrogen gas separated by the hydrogen separator 26. In the desulfurization reactor 10, sulfur components included in a natural gas are converted into hydrogen sulfide by the action of a hydrodesulfurization catalyst under the existence of a hydrogen gas, and is adsorbed and removed by, for example, ZnO .

The desulfurized natural gas is supplied to the reformer 12 after the carbon dioxide (CO_2) gas supplied from a carbon-dioxide supply source (not shown) and the steam generated in the waste heat boiler 14 are mixed. The reformer 12 reforms the natural gas by the steam and carbon-dioxide-gas reforming method using a carbon dioxide and a steam to produce a high-temperature synthesis gas including a carbon monoxide gas and a hydrogen gas as main components.

[0029] The high-temperature synthesis gas (for example, 900°C , 2.0 MPaG) produced in the reformer 12 in this way is supplied to the waste heat boiler 14, and is cooled down by the heat exchange with the water which circulates through the waste heat boiler 14 (for example, 400°C). Then, the water heated by the heat exchange becomes a high-pressure steam, and consequently, the waste heat is recovered.

The synthesis gas cooled down in the waste heat boiler 14 is supplied to the absorption tower 22 of the CO_2 removal unit 20, or the bubble column reactor 30, after condensate components are separated and removed from the synthesis gas in the vapor-liquid separator 18. The absorption tower 22 absorbs a carbon dioxide gas included in the synthesis gas within the absorbent contained therein, to separate the carbon dioxide gas from the synthesis gas. The absorbent including the carbon dioxide gas within this absorption tower 22 is introduced into the regeneration tower 24, the absorbent including the carbon dioxide gas is heated and subjected to a stripping treatment with, for example, a steam, and the resulting diffused carbon dioxide gas is supplied to the reformer 12 from the regeneration tower 24, and is reused for the above reforming reaction.

[0030] The synthesis gas produced in the synthesis gas production unit 3 in this way is supplied to the bubble column reactor 30 of the above FT synthesis unit 5. At this time, the composition ratio of the synthesis gas supplied to the bubble tower reactor 30 is adjusted to a composition ratio (for example, $\text{H}_2:\text{CO}=2:1$ (molar ratio)) suitable for FT synthesis reaction.

[0031] Additionally, the hydrogen separator 26 separates the hydrogen gas included in the synthesis gas, by the adsorption and desorption (hydrogen PSA) utilizing a pressure difference. This separated hydrogen gas is continuously supplied from a gas holder (not shown) or the like via a compressor (not shown) to various hydrogen-utilizing reaction devices (for example, the desulfurization reactor 10, the wax fraction hydrocracking reactor 50, the middle distillate hydrotreating reactor 52, the naphtha fraction hydrotreating reactor 54, etc.) which perform predetermined reactions utilizing hydrogen gas within the liquid fuel synthesizing system 1.

[0032] Next, the above FT synthesis unit 5 synthesizes liquid hydrocarbons by the FT synthesis reaction from the synthesis gas produced in the above synthesis gas production unit 3.

[0033] The synthesis gas produced in the above synthesis gas production unit 3 flows into the bottom of the bubble column reactor 30, and flows up in the slurry contained in the bubble column reactor 30. At this time, within the bubble column reactor 30, the carbon monoxide and hydrogen gas which are included in the synthesis gas react with each other by the FT synthesis reaction, thereby synthesizing hydrocarbons. The liquid hydrocarbons synthesized in the bubble column reactor 30 are introduced into the separator 36 along with catalyst particles as slurry.

[0034] The separator 36 separates the slurry into a solid component, such as catalyst particles, and a liquid component including liquid hydrocarbons. A portion of the separated solid component, such as the catalyst particles, is returned to the bubble column reactor 30, and a liquid component is supplied to the first fractionator 40. Additionally, the unreacted synthesis gas, and the hydrocarbons which are generated by the FT synthesis reaction and are gaseous under the conditions within the bubble column reactor 30, are introduced into the vapor-liquid separator 38 from the top of the bubble column reactor 30. The vapor-liquid separator 38 cools down these gases to separate condensed liquid hydrocarbons to introduce them into the first fractionator 40. Meanwhile, the gas component separated by the vapor-liquid separator 38, i.e., a mixed gas including the unreacted synthesis gas (CO and H_2), and hydrocarbon gas with a low carbon number (C_4 or less) as main components are recycled to the bubble column reactor 30, and the unreacted synthesis gas included in the mixed gas is subjected to the FT synthesis reaction again. In addition, for the purpose of preventing gaseous hydrocarbons composed mainly of C_4 or less from being accumulated at high concentration within an FT synthesis reaction system due to the recycling of the mixed gas, some of the mixed gas is not recycled to the bubble column reactor 30, but is introduced into an external combustion facility (a flare stack (not shown)), and is

combusted, and then emitted to the atmosphere.

[0035] Next, the first fractionator 40 fractionates the FT synthesis reaction product including the liquid hydrocarbons, which is supplied via the separator 36 and the vapor-liquid separator 38 from the bubble column reactor 30 as described above, as main components, into a naphtha fraction (whose boiling point is lower than about 150 °C), a middle distillate equivalent to kerosene and gas oil (whose boiling point is about 150 to 350 °C), and a wax fraction (whose boiling point exceeds about 350 °C).

The wax fraction (mainly C₂₁ or more) drawn from the bottom of the first fractionator 40 is brought to the wax fraction hydrocracking reactor 50, the middle distillate (mainly C₁₁ to C₂₀) drawn from the middle part of the first fractionator 40 is brought to the middle distillate hydrotreating reactor 52, and the naphtha fraction (mainly C₅ to C₁₀) drawn from the upper part of the first fractionator 40 is brought to the naphtha fraction hydrotreating reactor 54.

[0036] The wax fraction hydrocracking reactor 50 hydrocracks the wax fraction (approximately C₂₁ or more), which has been drawn from the bottom of the first fractionator 40, by using the hydrogen gas supplied from the above hydrogen separator 26, to convert the wax fraction into hydrocarbons of C₂₀ or less. In this hydrocracking reaction, the wax fraction is converted into hydrocarbons with a small carbon number by cleaving C-C bonds of hydrocarbons with a large carbon number, using a catalyst and heat. A product including the liquid hydrocarbons hydrocracked in this wax fraction hydrocracking reactor 50 is separated into gas and liquid in the vapor-liquid separator 56, the liquid hydrocarbons of which are brought to the second fractionator 70, and the gas component (including a hydrogen gas) of which is brought to the middle distillate hydrotreating reactor 52 and the naphtha fraction hydrotreating reactor 54 where the hydrogen gas is reused.

[0037] The middle distillate hydrotreating reactor 52 hydrotreats and hydroisomerize liquid hydrocarbons of the middle distillate (approximately C₁₁ to C₂₀), which have been brought out from the middle part of the first fractionator 40, by using the hydrogen gas supplied via the wax fraction hydrocracking reactor 50 from the hydrogen separator 26. A product including the hydrotreated liquid hydrocarbons is separated into vapor and liquid in the vapor-liquid separator 58, the liquid hydrocarbons of which are brought to the second fractionator 70, and the gas component (including hydrogen gas) of which is reused for the above hydrogenation reaction.

[0038] The naphtha fraction hydrotreating reactor 54 hydrotreats liquid hydrocarbons of the naphtha fraction with a low carbon number (approximately C₁₀ or less), which have been brought out from the top of the first fractionator 40, by using the hydrogen gas supplied via the wax fraction hydrocracking reactor 50 from the hydrogen separator 26. A product including the hydrotreated liquid hydrocarbons (hydrotreated naphtha) is separated into vapor and liquid in the vapor-liquid separator 60, the liquid hydrocarbons of which are brought to the naphtha stabilizer 72, and the gas component (including hydrogen gas) of which is reused for the above hydrogenation reaction.

[0039] Next, the second fractionator 70 fractionates the liquid hydrocarbons, which are supplied from the wax fraction hydrocracking reactor 50 and the middle distillate hydrotreating reactor 52 as described above, into hydrocarbons of C₁₀ or less (whose boiling point is lower than about 150 °C), a kerosene fraction (whose boiling point is about 150 to 250 °C), a gas oil fraction (whose boiling point is about 250 to 350 °C), and a so-called uncracked wax fraction (whose boiling point exceeds about 350 °C) which is not subjected to sufficient hydrocracking in the wax fraction hydrocracking reactor 50. The uncracked wax fraction is brought out from the bottom of the second fractionator 70, and this is recycled to the upstream of the wax fraction hydrocracking reactor 50 and is supplied to the wax fraction hydrocracking reactor 50 again. The kerosene fraction and the gas oil fraction are brought out from the middle part of the second fractionator 70. Meanwhile, hydrocarbons of C₁₀ or less is brought out from the top of the second fractionator 70, and is supplied to the naphtha stabilizer 72.

[0040] Moreover, the naphtha stabilizer 72 rectifies the hydrocarbons of C₁₀ or less, which have been supplied from the above naphtha fraction hydrotreating reactor 54 and the top of the second fractionator 70, and obtains high-purity naphtha (C₅ to C₁₀) as a product from the bottom. Meanwhile, a gas other than target products, including hydrocarbons of C₄ or less as a main component, is discharged from the top of the naphtha stabilizer 72. Additionally, this gas is introduced into an external combustion facility (not shown), is combusted therein, and is then emitted to the atmosphere.

[0041] The process (GTL process) of the liquid-fuel synthesizing system 1 has been described hitherto. By the GTL process concerned, a natural gas is converted into liquid fuels, such as high-purity naphtha (C₅ to C₁₀), kerosene (C₁₁ to C₁₅), and gas oil (C₁₆ to C₂₀).

[0042] Next, the configuration and operation of the surroundings of the middle distillate hydrotreating reactor 52 will be described in detail with reference to FIG 2.

This middle distillate hydrotreating reactor 52 includes a supply line 101 connected to the middle part of the first fractionator 40, a discharge line 102 which discharges a middle distillate hydrotreated in the middle distillate hydrotreating reactor 52, a sampling unit 103 which takes the sample of the hydrotreated middle distillate from the discharge line 102, a cloud point measuring unit 110 which measures the cloud point of the obtained sample of the hydrotreated middle distillate, and a control unit 104 which controls the operating conditions (hydrogen partial pressure/reaction temperature/throughput of middle distillate per unit time (for example, LHSV)) of the middle distillate hydrotreating reactor 52.

[0043] A middle distillate hydrotreating process to which the operation method of the middle distillate hydrotreating

reactor of the present embodiment is applied is a process to hydrotreat and hydroisomerize the middle distillate obtained by the FT synthesis reaction. In the FT synthesis reaction, other than saturated hydrocarbons which are a main product, olefins and oxygen-containing compounds such as alcohols including an oxygen atom originated from a carbon monoxide, are produced as by-products, and these by-products are also included in a middle distillate obtained by fractionating the FT synthesis oil. The hydrotreating in the middle distillate hydrotreating process mainly includes a reaction in which the olefins are hydrogenated and are converted into saturated hydrocarbons (paraffin hydrocarbons), and a reaction in which the oxygen-containing compounds are hydrodeoxygenated, and are converted into saturated hydrocarbons and water. As a catalyst which is effective in this hydrotreating, a catalyst including a metal component having hydrogenation ability as an active site is used.

Meanwhile, the hydroisomerization in the middle distillate hydrotreating process is a reaction in which normal paraffins included in the middle distillate are converted into isoparaffins. As a catalyst which is effective in this hydroisomerization, a catalyst composed of a metal component having hydrogenation/dehydrogenation ability, and a solid acid component is used. First, a normal paraffin is dehydrogenated into an olefin by the action of a metal component, and this olefin is skeleton-isomerized by the action of a solid acid component, and is hydrogenated by the action of the metal component, and is converted into an isoparaffin.

In the middle distillate hydrotreating process, both a catalyst effective in the hydrotreating and a catalyst effective in the hydroisomerization may be used. However, since the catalyst effective in the hydroisomerization is generally effective even in the hydrotreating, it is efficient and preferable to use the catalyst effective in the hydroisomerization.

[0044] Although the type of the middle distillate hydrotreating reactor according to the present invention is not limited, it is preferable that the reactor is a fixed-bed continuous flow type reactor. A single reactor may be adopted, and a plurality of reactors which is arranged in series or in parallel may be adopted. Additionally, a single catalyst bed may be provided within a reactor, and a plurality of divided catalyst beds may be used.

[0045] As a catalyst to be charged into the middle distillate hydrotreating reactor, a catalyst generally used for hydrotreating and/or hydroisomerization in petroleum refining, or the like, i.e., a catalyst in which an active metal having hydrogenation (dehydrogenation) ability is carried in an inorganic support, can be used.

As active metals which constitute the catalyst, one or more kinds of metals selected from a group consisting of metals belonging to the 6th group, the 8th group, the 9th group, and the 10th group on the periodic table of elements, are used. Concrete examples of such metals include noble metals, such as platinum, palladium, rhodium, ruthenium, iridium, and osmium, or cobalt, nickel, molybdenum, tungsten, iron, or the like, preferably includes platinum, palladium, nickel, cobalt, molybdenum, and tungsten, and more preferably includes platinum and palladium. Additionally, such metals are preferably used by combining two or more kinds thereof. Preferable combinations in that case include platinum-palladium, cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum, nickel-tungsten, or the like. Additionally, in a case where combinations, such as cobalt-molybdenum, nickel-molybdenum, nickel-cobalt molybdenum, nickel-tungsten, or the like, are used as the active metals, these combinations may be sulfurated by a sulfur compound before a catalyst is provided to the hydrotreating. In addition, the periodic table of elements means the long period type periodic table of elements based on the regulations of IUPAC (International Union of Pure and Applied Chemistry).

[0046] The inorganic support which constitutes the catalyst includes, for example, metal oxides, such as alumina, silica, titania, zirconia, and boria. These metal oxides may be one kind of metal or two kinds of mixtures, or may be composite metal oxides, such as silica-alumina, silica-zirconia, alumina-zirconia, and alumina-boria. The inorganic support is preferably composite metal oxides having solid acidity, such as silica-alumina, silica-zirconia, alumina-zirconia, and alumina-boria, from the viewpoint that the hydroisomerization of the normal paraffins efficiently proceeds simultaneously with the hydrotreating. Additionally, a small amount of zeolite may also be included in the inorganic support. Moreover, a binder may be blended with the inorganic support for the purpose of improvement of the moldability and mechanical strength of the support.

Preferable binders include alumina, silica, magnesia, or the like.

[0047] In a case where the active metal is the above noble metals, the content of the active metal in the catalyst is preferably about 0.1 to 3 mass % based on the mass of a support as metal atoms. Additionally, in a case where the active metal is a metal other than the above noble metals, the content of the active metal in the catalyst is preferably about 2 to 50 mass % based on the mass of a support as a metal oxide. In a case where the content of the active metal is less than the lower limit, the hydrotreating and the hydroisomerization tend to proceed insufficiently. On the other hand, in a case where the content of the active metal exceeds the upper limit, the dispersion of the active metal tends to deteriorate, and thus, the activity of the catalyst tends to decrease. Consequently, the catalyst cost increases.

[0048] The reaction temperature in the middle distillate hydrotreating reactor 52 in present embodiment is 180 to 400 °C, preferably 280 to 350 °C, and more preferably, 300 to 340°C. Here, the reaction temperature means the mean temperature of a catalyst bed in the middle distillate hydrotreating reactor 52. If the reaction temperature is higher than or equal to the lower limit temperature, the middle distillate is sufficiently hydrotreated and hydroisomerized, and if the

reaction temperature is lower than or equal to the upper limit temperature, the concurrence of the decomposition reaction of the middle distillate can be suppressed, and a decrease in the lifetime of the catalyst is suppressed.

[0049] The pressure (hydrogen partial pressure) in the middle distillate hydrotreating reactor 52 is preferably 0.5 to 12 MPa, and more preferably 1 to 5 MPa. If the pressure of the hydrotreating reactor is higher than or equal to 0.5 MPa, a raw middle distillate fraction is sufficiently hydrotreated, and if the pressure is lower than or equal to 12 MPa, the facility cost for increasing the resistance to pressure of the facility can be suppressed.

[0050] The liquid hourly space velocity (LHSV) in the middle distillate hydrotreating reactor 52 is preferably 0.1 to 10 h^{-1} , and more preferably 0.3 to 3.5 h^{-1} . If LHSV is greater than or equal to 0.1 h^{-1} , it is not necessary to make the volume of a reactor excessively large, and if the LHSV is equal to and less than 10 h^{-1} , the middle distillate is efficiently hydrotreated and hydroisomerized.

[0051] The hydrogen gas/oil ratio in the middle distillate hydrotreating reactor 52 is preferably 50 to 1000 NL/L, and more preferably 70 to 800 NL/L. Here, "NL" means the hydrogen volume (L) in the standard condition (0 °C and 101325 Pa). If the hydrogen gas/oil ratio is greater than or equal to 50 NL/L, the middle distillate is sufficiently hydrotreated and hydroisomerized, and if the hydrogen gas/oil ratio is less than or equal to 1000 NL/L, a facility for supplying a large amount of hydrogen gas becomes unnecessary, and an increase in operation cost can be suppressed.

[0052] In addition, the above reaction conditions in the middle distillate hydrotreating reactor 52 are determined based on a measured cloud point of the hydrotreated middle distillate which flows out of the reactor.

[0053] In the sampling unit 103, a sample of the hydrotreated middle distillate may be manually put into a container, the obtained sample may be carried to an independent cloud point measuring unit, and measurement of the cloud point may be manually performed. In that case, the sampling unit 103 can be composed, for example, by doubly installing manual valves at piping which have branched off from the discharge line 102.

[0054] On the other hand, the sampling unit 103 and the cloud point measuring unit 110 may have the configurations in which taking of the sample and the measurement of the cloud point are performed not manually but automatically, respectively. The sampling unit 103 in that case, for example, is composed of small-diameter piping which branches off from the discharge line 102 and returns to the discharge line 102 again, a plurality of valves which is installed along the piping to switch a flow line whose opening and closing are controlled based on time, and a control mechanism which controls the opening and closing of the valves based on time. A small amount of newly produced hydrotreated middle distillate always flows through the inside of the sampling unit 103, and a fixed amount of the sample is periodically taken by switching the valves. The sampling unit 103 and the cloud point measuring unit 110 are connected together by piping, and the sample obtained by the sampling unit 103 is automatically transferred to the cloud point measuring unit 110. Then, the cloud point measuring unit 110 automatically measures the cloud point of the transferred sample by interlocking the control of the valve of the sampling unit 103 with the control of the cloud point measuring unit 110. When the measurement of the cloud point is completed, the measurement result is displayed on a display device, for example, provided in a control console of the control unit 104 which controls the operation of the middle distillate hydrotreating reactor 52. Additionally, in the cloud point measuring unit 110, the sample of the hydrotreated middle distillate whose measurement is completed is automatically discharged, and preparation of the next measurement is performed.

[0055] As shown in FIG. 3, the cloud point measuring unit 110 includes a vessel body 111 in a bottomed cylindrical shape made of aluminum, a lid portion 112 which closes up an opening of the vessel body 111, a cooler 113 which cools the vessel body 111, a vessel temperature sensor 114 which measures the temperature of the vessel body 111, a liquid temperature sensor 115 which measures the temperature of the sample charged into the vessel body 111, and a cloud detector 116 which detects the cloud of the sample charged into the vessel body 111.

The cooler 113, which is an electronic cooling unit using a Peltier device (not shown), has the configurations to be able to control a cooling rate. Additionally, the cloud detector 116 is composed of an optical sensor including a photo-transmitter and a photo-receiver.

[0056] A cloud point measuring method in this cloud point measuring unit 110 will be described.

First, a obtained sample of the hydrotreated middle distillate is introduced into the vessel 111. Then, while the temperature is measured by the vessel temperature sensor 114 and the liquid temperature sensor 115, the hydrotreated middle distillate is cooled at a predetermined cooling rate by the cooler 113, and the liquid temperature when the generation of cloud has been detected by the cloud detector 116 is determined as the cloud point.

Here, it is preferable that the cloud point is measured while the obtained sample of the hydrotreated middle distillate is being cooled by the cooler 113 under the condition of a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less. In the present embodiment, the cooling rate is set to 9.5 °C/min.

[0057] Next, the operation method of the middle distillate hydrotreating reactor 52 will be described using the flow chart of FIG 4.

A raw middle distillate distilled from the middle part of the first fractionator 40 is supplied to the middle distillate hydrotreating reactor 52 through the supply line 101, and is hydrotreated and hydroisomerized in the reactor (S1).

The initial operating conditions of the reactor are set at the starting of the middle distillate hydrotreating reactor 52. Additionally, during normal operations, the operating conditions of the reactor are changed if the measured cloud point

of the hydrotreated middle distillate in the subsequent steps is out of a target range (S2).

[0058] The hydrotreated middle distillate flowing the discharge line 102 from the middle distillate hydrotreating reactor 52 is sampled (S3).

The cloud point of the sampled hydrotreated middle distillate is measured by the above-mentioned cloud point measuring unit 110 (S4).

Then, the measured cloud point, and an operation control target value are compared with each other, and whether or not the measurement value is within an operation control target range is judged (S5).

If the cloud point is within the operation control target range, the operating conditions of the middle distillate hydrotreating reactor 52 are maintained (S6). In addition, even in a case where the cloud point is within the operation control target range, minute changes in the operating conditions may be performed, for example, for the purpose of bringing the cloud point close to an operation control target center value.

Then, confirmation/maintenance of a stable state becomes possible by performing sampling of the hydrotreated middle distillate again after a predetermined period of time (returns to S3), and repeating the subsequent steps.

On the other hand, if the cloud point is out of the operation control target range, in the control unit 104, the operating conditions (hydrogen partial pressure/reaction temperature/throughput of middle distillate per unit time (for example, LHSV)) of the middle distillate hydrotreating reactor 52 are changed (returns to S2).

Then, sampling of the hydrotreated middle distillate is performed again after predetermined time (S3), and the subsequent steps are repeated. This makes it possible to confirm the effects of changes in the operating conditions of the middle distillate hydrotreating reactor 52 in S2.

[0059] As for changes in the operating conditions of the middle distillate hydrotreating reactor 52 in S2, specifically, if the cloud point exceeds the upper limit of the operation control target range, the hydroisomerization is promoted and the cloud point of the hydrotreated middle distillate is lowered, by setting the conditions wherein the hydrogen partial pressure is raised, and/or the reaction temperature is raised, and/or the throughput of the middle distillate per unit time (LHSV) is reduced. Additionally, if the cloud point falls below the lower limit of the operation control target range, the hydroisomerization is suppressed and the cloud point of the hydrotreated middle distillate is elevated by setting the conditions wherein the hydrogen partial pressure is reduced, and/or the reaction temperature is lowered, and/or the throughput of the middle distillate per unit time (LHSV) is increased. Especially, by changing the reaction temperature, the cloud point of the hydrotreated middle distillate can be effectively changed.

In addition, the control unit which controls the operating conditions of the middle distillate hydrogenation reactor 52, such as hydrogen partial pressure, reaction temperature, and throughput of the middle distillate per unit time, may be the one which performs the operation control of a general reactor.

[0060] If the cloud point of the hydrotreated middle distillate which flows out of the middle distillate hydrotreating reactor 52 is out of the operation control target range, the operating conditions of the reactor are changed so that the cloud point falls within the operation control target range. Then, the handling of a hydrotreated middle distillate which flows out until it is confirmed that the cloud point of the hydrotreated middle distillate which flows out has fallen within the operation control target range is not particularly limited.

If the cloud point of the hydrotreating middle distillate which flows out of the middle distillate hydrotreating reactor 52 falls below the lower limit of the operation control target range, even if there is a problem in terms of efficiency that the yield of the middle distillate is lowered due to an increase in a light component caused by a concurrent decomposition reaction, there is a possibility that a middle distillate product obtained through the fractionation in the second fractionator 70 satisfies product specifications. Thus, the hydrotreated middle distillate may be brought to the second fractionator 70, and may be taken out as a product.

On the other hand, if the cloud point of the hydrotreated middle distillate which flows out of the middle distillate hydrotreating reactor 52 exceeds the upper limit of the operation control target range, the hydrotreated middle distillate may not be brought to the second fractionator 70, but may be brought to a slop tank. Otherwise, after the hydrotreated middle distillate is temporarily stored in another storage facility, the middle distillate is returned to and reprocessed separately in the middle distillate hydrogenation reactor 52. Then, after it is confirmed that the cloud point has fallen within the operation control target range, the hydrotreated middle distillate may be brought to the second fractionator 70 and may be taken out as a product.

Additionally, not only the hydrotreated middle distillate from the middle distillate hydrotreating reactor 52 but a hydrocracked product from the wax fraction hydrocracking reactor 50 is supplied to the second fractionator 70. Hence, even in a case where the cloud point of the hydrotreated middle distillate which flows out of the middle distillate hydrotreating reactor 52 exceeds the upper limit of the operation control target range, the cloud point of a middle distillate product obtained from the second fractionator 70 may satisfy the product specifications. Accordingly, if the hydrotreated middle distillate is brought to and fractionated in the second fractionator 20, and if it is expected that the middle distillate obtained satisfies the product specifications, this may be taken out as a product. If the cloud point of the product exceeds the upper limit of the range of the product specifications, the product may be returned to and reprocessed in the middle distillate hydrotreating reactor 52.

[0061] According to the middle distillate hydrotreating reactor 52 and the operation method of the middle distillate hydrotreating reactor 52 constructed as described above, which are the present embodiment, the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor 52 is measured, and the operating conditions of the middle distillate hydrotreating reactor 52 are controlled based on this cloud point. Thus, the degree of the hydroisomerization in the middle distillate hydrotreating reactor 52 is constantly maintained. Hence, the properties of the produced hydrotreated middle distillate become stable, and thus, the quality of gas oil (diesel fuel oil) produced using this hydrotreated middle distillate as a feedstock can be significantly improved.

[0062] Additionally, since the sampled hydrotreated middle distillate is cooled by the cooler 113 composed of an electronic cooling unit using the Peltier device in the cloud point measurement, it is possible to control the cooling rate of the hydrotreated middle distillate accurately and easily. Also, in the present embodiment, the cooling rate is set to 5.0 °C/min or more and 15.0 °C/min or less, and more specifically, the cooling rate is set to 9.5°C/min. Thus, it is possible to accurately and rapidly measure the cloud point. This makes it possible to control the operating conditions by the control unit 104 with suitable timing, and to stabilize the operation of the middle distillate hydrotreating reactor 52.

[0063] Although the embodiments of the present invention have been described hitherto in detail with reference to the drawings, concrete configurations are not limited to the embodiments, and the present invention also includes design changes which do not depart from the spirit of the present invention. For example, although the cloud point measuring unit has been described as one including the cooler composed of the electronic cooling unit using the Peltier device, the invention is not limited thereto. For example, as shown in JIS K 2269, the cloud point may be measured by gradually cooling the hydrotreated middle distillate using a cooling bath.

Additionally, the operating conditions of the upgrading unit, or the like, are not limited to the ranges described in the embodiment, and may be suitably changed according to situations.

Moreover, the configurations of the synthesis gas production unit 3, FT synthesis unit 5, and upgrading unit 7 are not limited to those described in the present embodiment, and it is only necessary to supply the middle distillate of the FT synthesis hydrocarbons to the middle distillate hydrotreating reactor 52.

[Embodiments]

[0064] The results of a confirmatory experiment performed to confirm the effects of the present invention will be described.

(Relationship between cloud point and degree of hydroisomerization)

[0065] A confirmatory experiment was performed on the relationship between the degree of the hydroisomerization in the middle distillate hydrotreating reactor, and the cloud point (CP) of a produced hydrotreated middle distillate. The operating conditions of the middle distillate hydrotreating reactor was changed, a plurality of several hydrotreated middle distillates with different cloud points were produced, and samples of the respective hydrotreated middle distillates were obtained. The cloud points of the respective hydrotreated middle distillates were measured by the cloud point measuring unit in the aforementioned embodiment in a condition of a cooling rate of 9.5°C/min. Additionally, as for the degree of the hydroisomerization in the middle distillate hydrotreating reactor when the samples of the respective hydrotreated middle distillates were obtained, the content of normal paraffins with a carbon number of 19 or more (n-C₁₉₊ content) in the respective samples obtained by component analysis was used as an index. The results when n-C₁₉₊ content and CP were plotted are shown in FIG 5.

[0066] As shown in FIG 5, a strong correlation is observed between the cloud points of the hydrotreated middle distillates, and n-C₁₉₊ content. Here, n-C₁₉₊ content is an index showing the degree of hydroisomerization. It was confirmed from this that the degree of the hydroisomerization in the middle distillate hydrotreating reactor can be understood by measuring the cloud points of the hydrotreated middle distillates.

(Measuring method of cloud point)

[0067] Next, confirmation was performed with regard to the precision and measuring time in the cloud point measurement when the measurement is performed by the measuring method based on JIS K 2269 and the measuring method shown in the present embodiment in which the hydrotreated middle distillate sample is cooled by the electronic cooling unit using the Peltier device at increased cooling rates.

Three kinds of samples (samples 1 to 3) of liquid hydrocarbons having a boiling point range equivalent to gas oil were prepared, and cloud points of these samples were measured by a measuring method based on JIS K 2269 using an automatic pour point/cloud point/cold filter plugging point tester RPCF-03CML (Trade name), made by Rigo Co., Ltd., and were referred to as Examples 1 to 3.

Additionally, the cloud points of the aforementioned samples were measured in conditions of cooling rates of 5.0 °C/min,

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7.0 °C/min, and 9.5 °C/min, respectively, by the cloud point measuring unit (specifically, an automatic pour point/cloud point tester MPC-102 Type made by Tanaka Scientific Ltd.) which is the above embodiment, and were referred to as Examples 4 to 12. In addition, in Examples 1 to 12, the identical cloud point measurement was repeated four times. The results are shown in Table 1.

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[Table 1]

	Examples 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Sample	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)	Sample (1)	Sample (2)	Sample (3)
Measuring Method	JIS K 2269	JIS K 2269	JIS K 2269	5 °C/min	5 °C/min	5 °C/min	7 °C/min	7 °C/min	7 °C/min	9.5 °C/min	9.5 °C/min	9.5 °C/min
Measurement Value (1)	-9	-18	-30	-8	-17	-30	-7	-17	-30	-7	-17	-30
Measurement Value (2)	-8	-17	-29	-8	-17	-30	-8	-17	-30	-7	-17	-30
Measurement Value (3)	-7	-17	-29	-8	-17	-30	-7	-17	-30	-7	-17	-30
Measurement Value (4)	-8	-18	-30	-7	-18	-30	-7	-17	-30	-6	-17	-30
Measuring Time	60 min	70 min	90 min	8min	12 min	21 min	7min	10 min	19 min	6 min	8min	17 min

[0069] As shown in Table 1, the cloud points measured by JIS K 2269, and the cloud points measured in conditions of cooling rates of 5.0 °C/min, 7.0 °C/min, and 9.5 °C/min, respectively, coincide with each other with an error within 2°C for the identical sample. Here, the error in JIS K 2269 is defined within 2°C for the identical testing device and is defined within 4°C for different testing devices. Then, the error within 2°C between Examples 1 to 3 and Examples 4 to 12 is within a range permitted even in JIS K 2269. It was confirmed that even Examples 4 to 12, measuring in conditions of cooling rates of 5.0 °C/min, 7.0 °C/min, and 9.5 °C/min, respectively, can measure the cloud points with the precision equivalent to JIS K 2269.

[0070] Additionally, the measuring time was 60 to 90 minutes in Examples 1 to 3 based on JIS K 2269, whereas the measuring time was 6 to 21 minutes, during which the cloud points could be measured in a short time, in Examples 4 to 12 measured in conditions of cooling rates of 5.0 °C/min, 7.0 °C/min, and 9.5 °C/min, respectively. Accordingly, it was confirmed that the control of the middle distillate hydrotreating reactor can be reliably and more rapidly performed by measuring the cloud points as in Examples 4 to 12.

[Industrial Applicability]

[0071] According to the operation method of the middle distillate hydrotreating reactor, and the middle distillate hydrotreating reactor in the present invention, it is possible to properly hydroisomerizes the FT synthesis hydrocarbons obtained by the FT synthesis reaction in the hydrotreating process of the middle distillate, to produce a hydrotreated middle distillate with stable properties, and to obtain high-quality gas oil.

[Description of Reference Numerals]

[0072]

1: LIQUID-FUEL SYNTHESIZING SYSTEM
 7: UPGRADING UNIT
 40: FIRST FRACTIONATOR
 52: MIDDLE DISTILLATE HYDROTREATING REACTOR
 103: SAMPLING UNIT
 104: CONTROL UNIT
 110: CLOUD POINT MEASURING UNIT
 113: COOLER
 116: CLOUD DETECTOR

Claims

1. An operation method of a middle distillate hydrotreating reactor which hydrotreats and hydroisomerizes a middle distillate including components of a boiling point range equivalent to gas oil among FT synthesis hydrocarbons synthesized by the Fisher-Tropsch synthesis reaction, the operation method comprising the steps of:

bringing the middle distillate into contact with a catalyst to hydrotreat and hydroisomerize the middle distillate to produce hydrotreated middle distillate;
 measuring the cloud point of the hydrotreated middle distillate flowing out from the middle distillate hydrotreating reactor; and
 controlling the operating conditions of the middle distillate hydrotreating reactor so that the cloud point comes to a predetermined target value.

2. The operation method of a middle distillate hydrotreating reactor according to Claim 1, wherein, in the step of measuring the cloud point, the cloud point is measured while cooling a obtained sample of the hydrotreated middle distillate at a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less.

3. The operation method of a middle distillate hydrotreating reactor according to Claim 1 or 2, wherein, in the step of measuring the cloud point, the cloud point is measured while cooling the obtained sample at the cooling rate controlled by an electronic cooling unit using a Peltier device.

4. The operation method of a middle distillate hydrotreating reactor according to any one of Claims 1 to 3, wherein, in the step of controlling the operating conditions of the middle distillate hydrotreating reactor, at least one

of hydrogen partial pressure, reaction temperature, and throughput of middle distillate per unit time is controlled.

- 5 **5.** A middle distillate hydrotreating reactor which hydrotreats and hydroisomerizes a middle distillate including a component of a boiling point range equivalent to gas oil among FT synthesis hydrocarbons synthesized by the Fisher-Tropsch synthesis reaction, the reactor comprising:

 a sampling unit which takes a sample of the produced hydrotreated middle distillate; and
 a cloud point measuring unit which measures the cloud point of the obtained sample.

- 10 **6.** The middle distillate hydrotreating reactor according to Claim 5,
 wherein the sampling unit is connected to the cloud point measuring unit by piping so as to automatically take the sample and transfer the sample to the cloud point measuring unit, and the cloud point measuring unit automatically measures the cloud point of the transferred sample.

- 15 **7.** The middle distillate hydrotreating reactor according to Claim 5 or 6,
 wherein, the cloud point measuring unit includes a cooler capable of cooling the obtained sample at a cooling rate of 5.0 °C/min or more and 15.0 °C/min or less.

- 20 **8.** The middle distillate hydrotreating reactor according to Claim 7, wherein the cooler is an electronic cooling unit using a Peltier device.

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FIG. 1

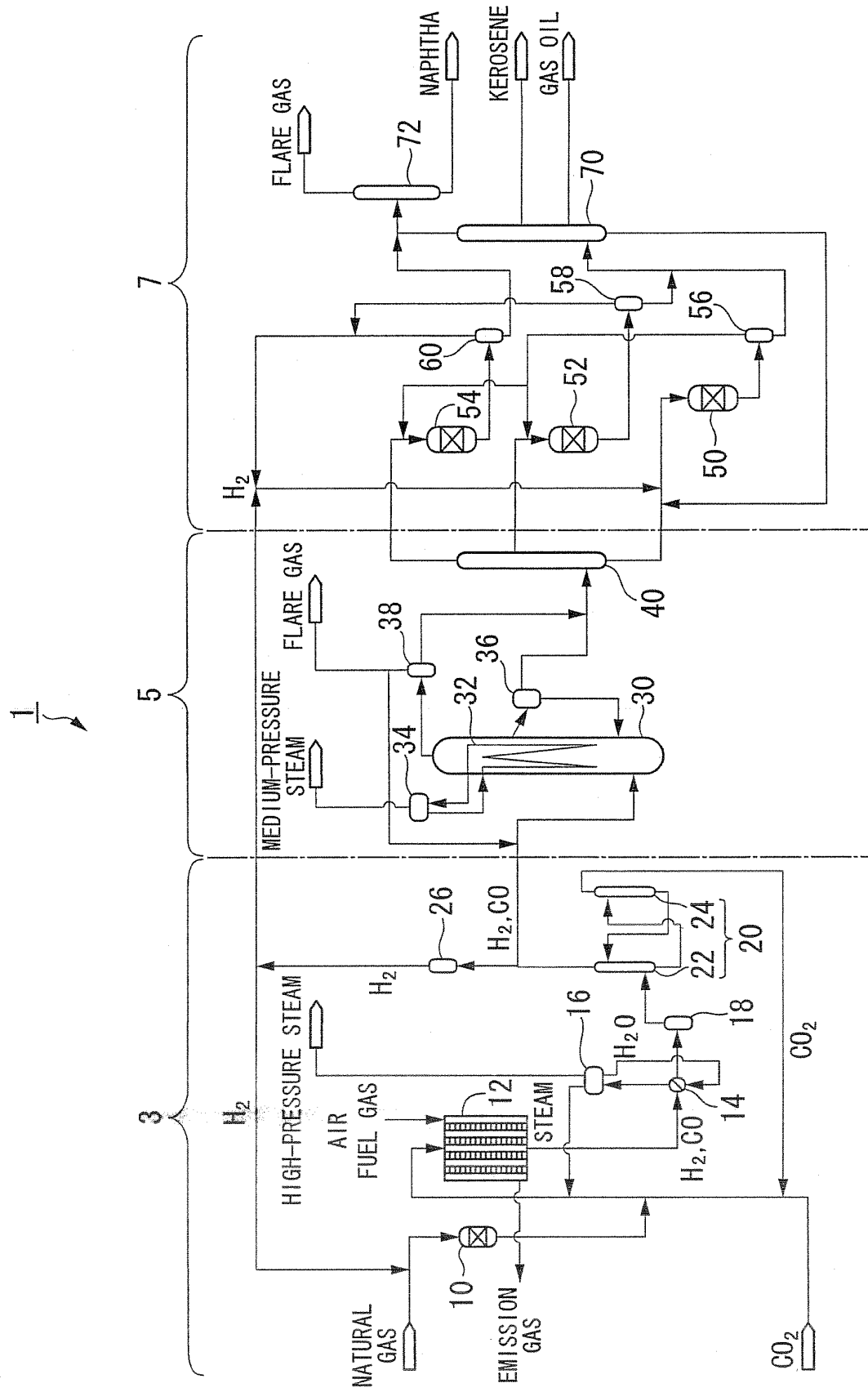


FIG. 2

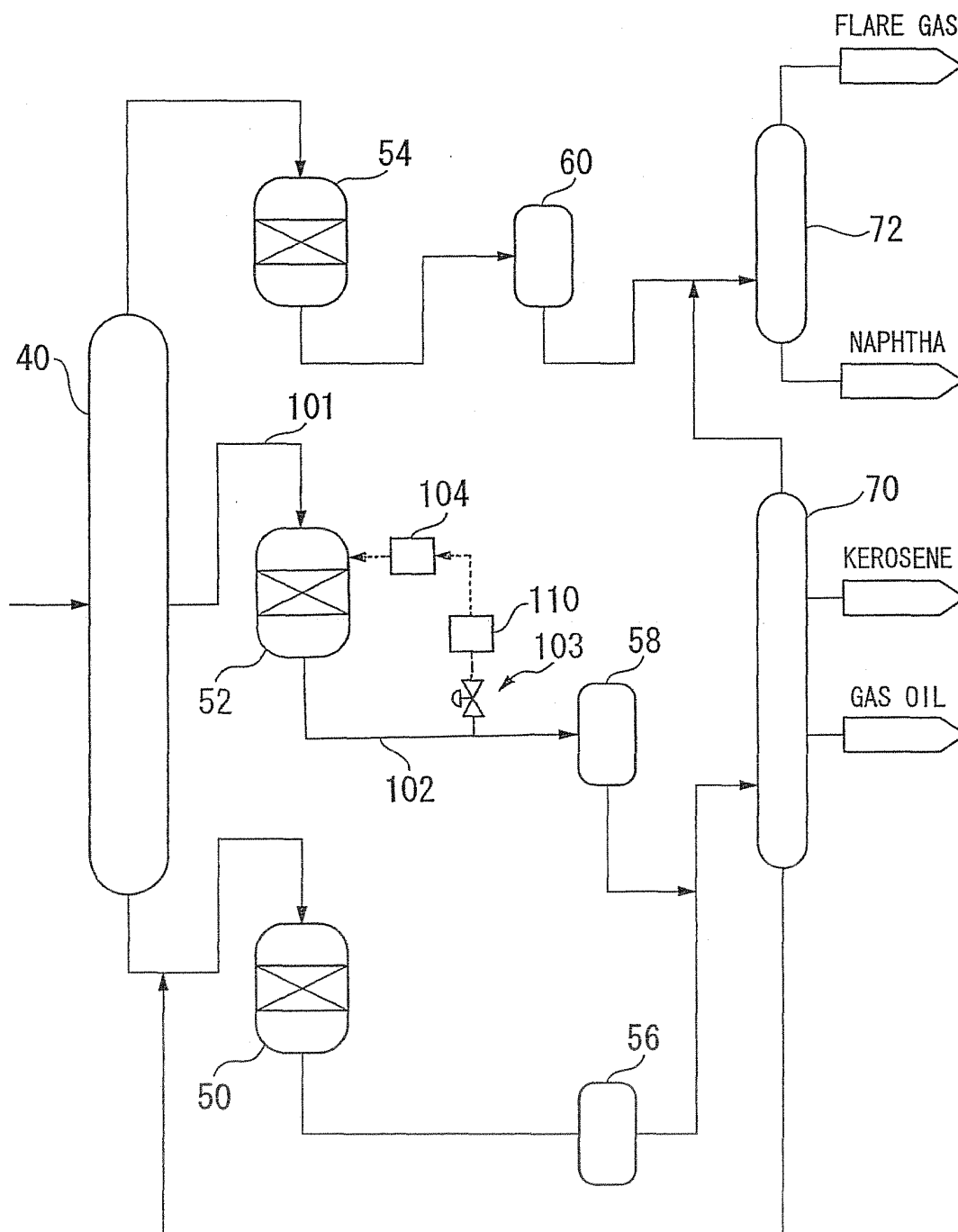


FIG. 3

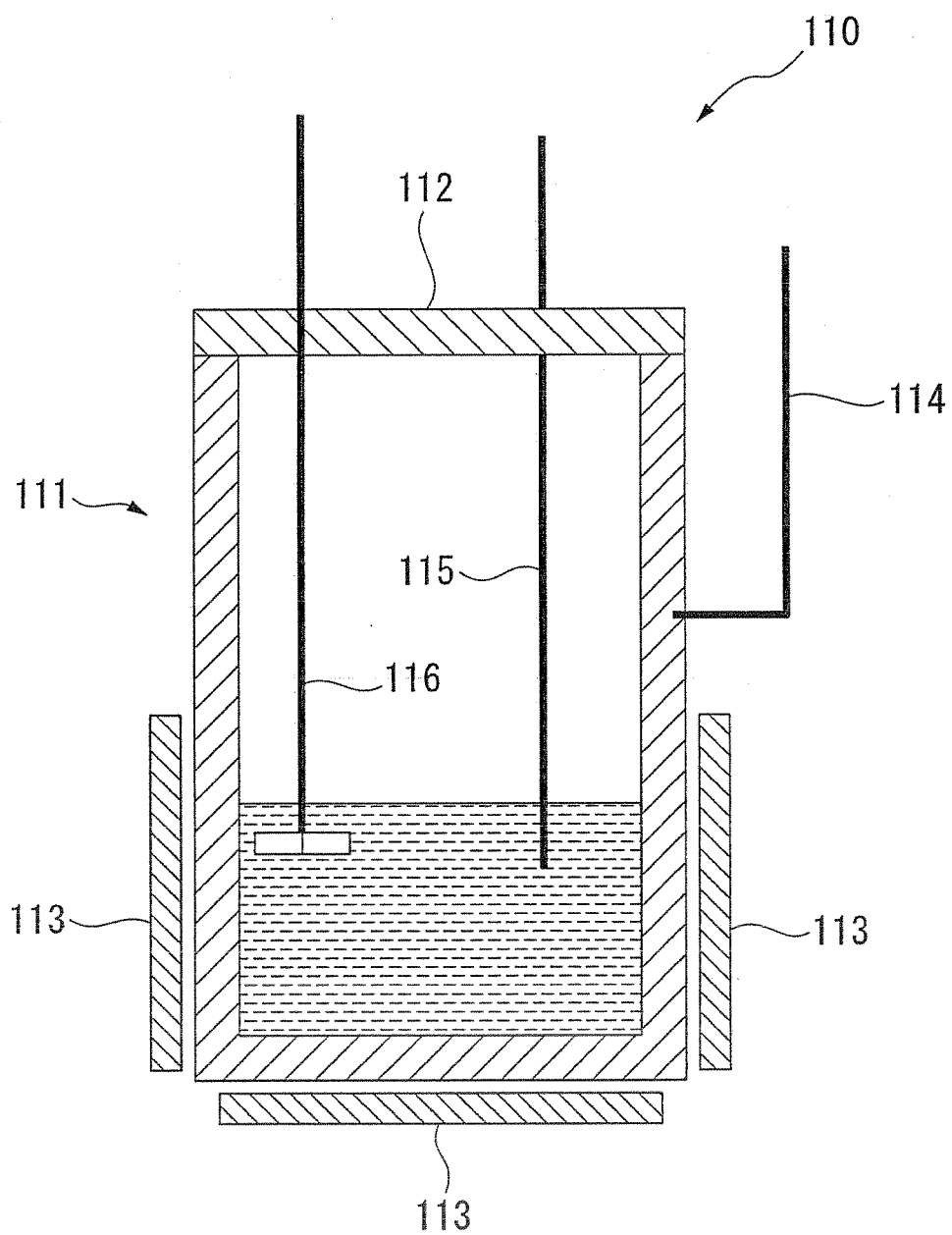


FIG. 4

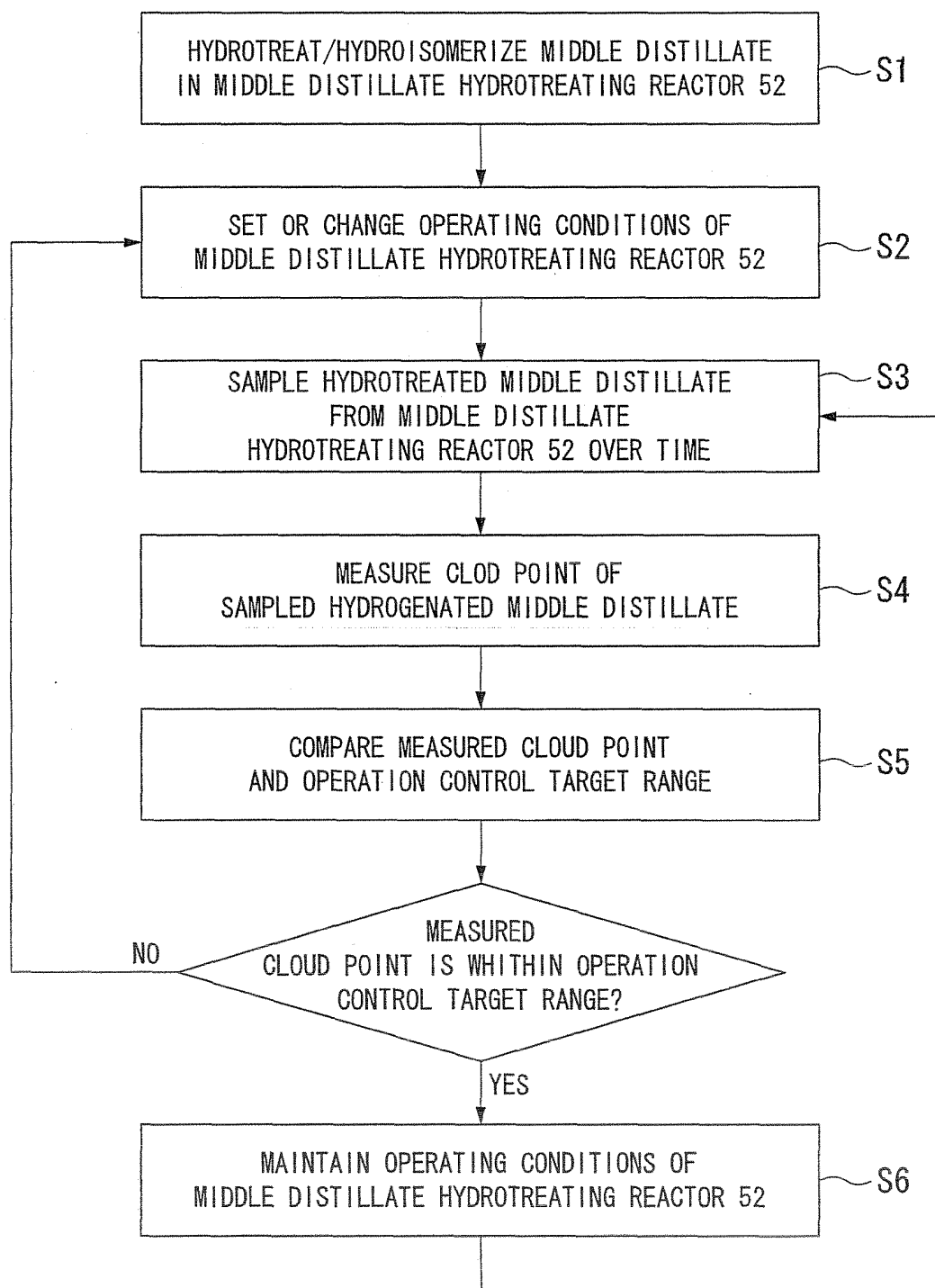
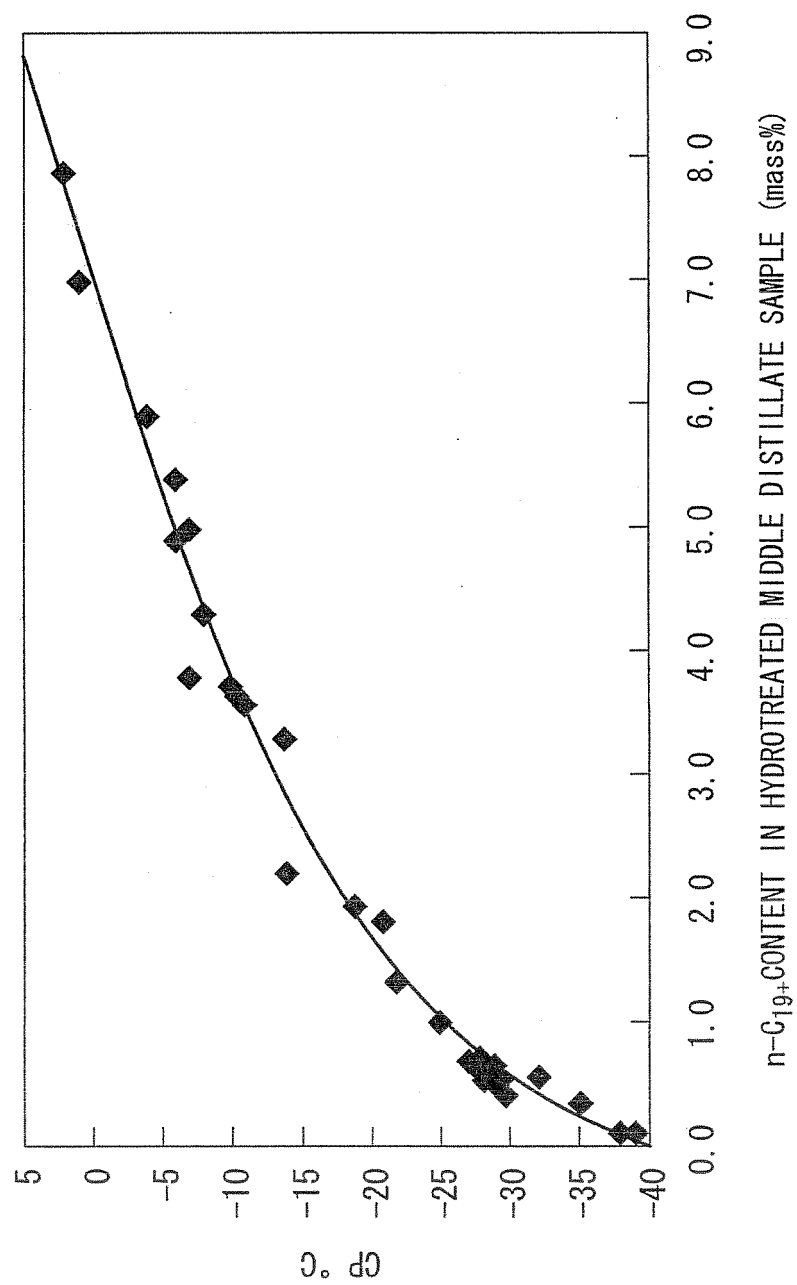


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/000340

A. CLASSIFICATION OF SUBJECT MATTER

C10G45/72(2006.01) i, C10G45/58(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G45/72, C10G45/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus (JDreamII), JST7580 (JDreamII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2007/094199 A1 (Nippon Oil Corp.), 23 August 2007 (23.08.2007), page 11, table 1 & JP 2007-211217 A	1, 4-6 2-3, 7-8
Y	JP 61-4948 A (Elf France), 10 January 1986 (10.01.1986), claim 8 & US 5007733 A & EP 171300 A1	2-3, 7-8



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

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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

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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

08 February, 2010 (08.02.10)

Date of mailing of the international search report

16 February, 2010 (16.02.10)

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REFERENCES CITED IN THE DESCRIPTION

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