METHOD FOR THE PRODUCTION OF SYNTHETIC FUEL

An object of the invention is to provide a method of producing synthetic fuel from Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method, the method comprising the steps of: (a) fractionating, in a fractionator, Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method into at least two fractions of a middle fraction containing a component having a boiling range corresponding to diesel fuel oil, and a wax fraction containing a wax component heavier than the middle fraction; (b) separating and removing a magnetic particle contained in the wax fraction obtained in the step (a) at 100°C to 450°C by using a high gradient magnetic separator; and (c) hydrocracking the wax fraction obtained in the step (b) from which the magnetic particle is separated and removed.

FIG. 2
The present invention relates to a method of producing synthetic fuel from Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method (hereinafter, simply referred to as "a FT synthesis method"). Specifically, the method of producing the synthetic fuel includes a step in which magnetic particles, contained in a wax fraction fractionated from the Fischer-Tropsch synthetic crude oil obtained by the FT synthesis method using carbon monoxide and hydrogen as raw materials, are separated by a magnetic separator.

BACKGROUND ART

In recent years, a clean and environmentally-friendly liquid fuel that contains a low content of sulfur and aromatic hydrocarbons and that is compatible with the environment has been required from the viewpoint of the reduction of environmental burdens. Therefore, in the oil industry, an FT synthesis method using raw materials such as carbon monoxide and hydrogen has been studied to develop a method of producing a clean liquid fuel. According to the FT synthesis method, a liquid fuel base stock containing a high content of paraffins but not containing sulfur (for example, a diesel fuel base stock) can be produced. For this reason, such an FT synthesis method has high expectations. For example, a clean liquid fuel compatible with the environment is proposed in Patent Document 1.


Meanwhile, the synthetic crude oil obtained by the FT synthesis method (hereinafter, referred to as "FT synthetic crude oil") has a broad carbon number distribution. Specifically, an FT naphtha fraction containing a high content of hydrocarbons having a boiling point of approximately less than 150°C, an FT middle fraction containing a high content of components having a boiling point in the range of from approximately 150°C to approximately 360°C, and an FT wax fraction heavier than the middle fraction can be obtained from the FT synthetic crude oil. In this case, a large amount of the FT wax fraction is produced therein. Accordingly, if the FT wax fraction obtained by fractionating the synthetic crude oil is hydrocracked to convert the FT wax fraction into the middle fraction, then, production of fuel oil such as diesel fuel can be increased.

Whereas, with regard to a catalyst used in the FT synthetic method using materials such as carbon monoxide and hydrogen, an iron solid catalyst has been frequently used in the conventional art. However, in recent years, a cobalt solid catalyst has been developed such a catalyst has high activity. In this case, the reaction mode of the FT synthesis method can be a fixed bed-type, a fluidized bed-type, a moving bed-type or the like. However, a heterogeneous catalyst which is a solid catalyst is used in any type of reaction.

DISCLOSURE OF THE INVENTION

PROBLEM THAT THE INVENTION IS TO SOLVE

As described above, a heterogeneous catalyst which is a solid catalyst is used in the FT synthesis method regardless of a mode of reaction. The obtained FT synthetic crude oil is subjected to a process of removing a catalyst remaining therein by use of an ordinary method such as filtering or settling. However, since the remaining catalyst cannot be completely removed due to cost, a portion of the catalyst is inevitably contained in the FT synthetic crude oil although the amount thereof is small. Then, the remaining catalyst is concentrated in the wax fraction that is a bottom component in fractionating the FT synthetic crude oil.

As a result, the remaining catalyst may be undesirably accumulated in a hydrocracking apparatus because, even though the concentration of remaining catalyst contained in the FT synthetic crude oil is low in the initial stages, the remaining catalyst is concentrated in the bottom of a fractionator.

MEANS FOR SOLVING THE PROBLEM

The present inventors discovered that such cobalt catalyst particles are particles having magnetism and that the cobalt catalyst particle can be magnetically separated in the same manner as iron catalyst particles that are catalysts remaining in FT synthetic crude oil. Thus, the present invention is achieved based on the discovery. Specifically, an aspect of the invention provides the following.

A method of producing synthetic fuel from Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method.
method, the method including the steps of: (a) fractionating, in a fractionator, Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method into at least two fractions of a middle fraction containing a component having a boiling range corresponding to diesel fuel oil, and a wax fraction containing a wax component heavier than the middle fraction; (b) separating and removing a magnetic particle contained in the wax fraction obtained in the step (a) at 100°C to 450°C by using a high gradient magnetic separator; and (c) hydrocracking the wax fraction obtained in the step (b) from which the magnetic particle is separated and removed.

[0009] [2] The method of producing synthetic fuel according to [1], wherein, in the step (b), a ferromagnetic filling material is disposed in a space where a magnetic field is generated inside the high gradient magnetic separator, the wax fraction obtained in the step (a) is introduced into the magnetic field space in the state where the magnetic field is generated to capture the magnetic particle to the ferromagnetic filling material, and then washing liquid is introduced into the space where the ferromagnetic filling material is disposed while eliminating the magnetic field to discharge the magnetic particle to the outside of the high gradient magnetic separator.

[3] The method of producing synthetic fuel according to [1] or [2], wherein, in the step (b) of separating and removing the magnetic particle using the high gradient magnetic separator is carried out in conditions where the magnetic field intensity is 1,500 Gauss or more and the liquid residence time is three seconds or more.

ADVANTAGE OF THE INVENTION

[0010] According to the present invention, magnetic particles are removed by magnetic separation whereby the magnetic particles can be prevented from being accumulated in the hydrocracking apparatus. Consequently, the hydrocracking apparatus can be operated without any trouble. Furthermore, when the magnetic field intensity and the liquid residence time are controlled in the above-described aspect of the invention, it is possible to more efficiently carry out the magnetic separation of the magnetic particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a schematic view showing a plant for producing fuel, including an FT synthesis reactor 10, a separator 20 for separating particles in FT synthetic crude oil, a first fractionator 30 for fractionating the FT synthetic crude oil into a naphtha fraction, a middle fraction, and a wax fraction, a high gradient magnetic separator 40 for removing magnetic particles in the wax fraction, a hydrotreating apparatus 54 and a hydroisomerizing apparatus 52 for respectively processing the naphtha fraction and the middle fraction, a hydrocracking apparatus 50 for hydrocracking the wax fraction from which the magnetic particle has been magnetically separated, and a second fractionator 60.

FIG. 2 is a schematic view showing the high gradient magnetic separator 40 used in the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

[0012] Hereinafter, the present invention will be described in detail. As shown in FIG. 1, synthetic gas containing carbon monoxide gas (CO) and hydrogen gas (H\textsubscript{2}) is supplied via a line 1, and liquid hydrocarbons are produced by an FT synthesis reaction in an FT synthesis reactor 10. The synthetic gas can be obtained, for example, by appropriately reforming a hydrocarbon. Typical examples of the hydrocarbon include methane, natural gas, LNG (liquid natural gas) or the like. For example, a partial oxidation reforming method (POX) using oxygen, an auto thermal reforming method (ATR) (e.g. the partial oxidation reforming method is combined with
[0014] Next, the FT synthesis will be described with reference to FIG. 1. The plant for producing fuel shown in FIG. 1 includes an FT synthesis reactor 10. The FT synthesis reactor 10 may be, for example, a bubble column reactor which is an example of a reactor for obtaining a liquid hydrocarbon by synthesizing synthetic gas. The FT synthesis reactor 10 functions as an FT synthesis reactor for obtaining the liquid hydrocarbon from the synthetic gas by an FT synthesis reaction.

[0015] The main body of the FT synthesis reactor 10 is a substantially cylindrical-shaped metallic vessel, and has a diameter of 1 m to 20 m and preferably of 2 m to 10 m. The reactor body has a height of 10 m to 50 m and preferably of 15 to 45 m. A slurry in which solid catalyst particles are suspended in liquid hydrocarbons (product of the FT synthesis reaction) is contained inside the main body.

A part of the slurry is flowed out from the middle of the FT synthesis reactor 10 into a separator 20 via a line 3. Unreacted synthetic gas or the like is discharged from the top of the FT synthesis reactor 10 through a line 2, and a part of the unreacted synthetic gas is suitably recycled to the FT synthesis reactor 10.

[0016] The synthetic gas supplied from the outside via a synthetic gas supply pipe 1 is injected from a synthetic gas supply port (not shown in FIG. 1) to the slurry contained in the FT synthesis reactor 10. When the synthetic gas comes into contact with the catalyst particles, a synthesis reaction (FT synthesis reaction) of the liquid hydrocarbon occurs due to the contact reaction. Specifically, as shown in the following chemical formula (1), a synthesis reaction occurs between hydrogen gas and carbon monoxide gas.

\[
2nH_2 + nCO \rightarrow (CH_2)_n + nH_2O \quad (1)
\]

[0017] Specifically, the synthetic gas is flowed into the bottom of the FT synthesis reactor 10 and moves upward in the slurry contained in the FT synthesis reactor 10. In this case, in the FT synthesis reactor 10, the reaction between the hydrogen gas and the carbon monoxide gas contained in the synthetic gas occurs in terms of the above-described FT synthesis reaction, thereby producing hydrocarbons. Additionally, heat is generated due to the synthesis reaction. However, such heat may be removed by use of a suitable cooling device.

The metallic catalyst may be a supported type, a deposition type or the like. However, the metallic catalyst is in a form of solid particle containing iron group metal even in any type. A sufficient amount of metal may be contained in the solid particles. However, 100% of the solid particle may be metal. As an example of the iron group metal, iron can be mentioned. However, cobalt is preferable in view of high activity.

[0018] The composition ratio of the synthetic gas supplied to the FT synthesis reactor 10 can be set to a composition ratio suitable for the FT synthesis reaction (for example, \( H_2:CO = 2:1 \) (molar ratio)). Additionally, the pressure of the synthetic gas supplied to the FT synthesis reactor 10 can be increased up to a pressure (for example, 3.6 M PaG) suitable for the FT synthesis reaction by use of a suitable compressor (not shown in FIG. 1). However, the compressor may not be provided in some cases.

[0019] The liquid hydrocarbon synthesized in the FT synthesis reactor 10 in this manner is extracted in a form of slurry having the suspended catalyst particles from the FT synthesis reactor 10 through the line 3 connected to the middle of the FT synthesis reactor 10, and is introduced into the separator 20. In the separator 20, the extracted slurry is separated into a solid component of catalyst particles, etc. and a liquid component containing the liquid hydrocarbons by use of a solid-liquid separation device. The solid-liquid separation device may be a device according to a known and common method. For example, a filtering device using a suitable filter such as a sintered metallic filter, a gravitational sedimentation separator (e.g. a spontaneous sedimentation type), a cyclone, a magnetic separator, a centrifugal separator, and the like can be mentioned.

[0020] The first fractionator 30 may fractionate the liquid hydrocarbons supplied from the FT synthesis reactor 10 in a form of slurry into a naphtha fraction, a middle fraction, and a wax fraction. The first fractionator 30 may fractionate the liquid hydrocarbons supplied from the FT synthesis reactor 10 in a form of slurry into three fractions. In this case, the liquid hydrocarbons may be divided into three fractions, e.g. the
Lightest naphtha fraction (having a boiling point of approximately less than 150°C), the middle fraction having a middle boiling range (a boiling point in the range of from approximately 150°C to approximately 350°C), and the heaviest wax fraction (having a boiling point of approximately more than 350°C). In FIG. 1, the liquid hydrocarbons are divided into three fractions. However, the liquid hydrocarbons may be divided into two fractions, e.g. the wax fraction and the sum of the other fractions, and also may be divided into three or more fractions including the wax fraction therein. 

[0024] Liquid hydrocarbons (mainly having twenty one or more carbon atoms) of the wax fraction extracted from the bottom of the first fractionator 30 is led to a high gradient magnetic separator 40, and then, is brought to the hydrocracking apparatus 50 for the wax fraction. Additionally, liquid hydrocarbons (mainly having eleven to twenty carbon atoms) of the middle fraction extracted via a line 32 connected to the middle portion of the first fractionator 30 is transferred to the hydroisomerizing apparatus 52 for the middle fraction. Liquid hydrocarbons (mainly having five to ten carbon atoms) of the naphtha fraction extracted from the top of the first fractionator 30 is brought to the hydrotreating apparatus 54 for the naphtha fraction.

[0025] After the wax fraction (mainly having twenty one or more carbon atoms) flowed from the bottom of the first fractionator 30 via a line 31 is treated in the high gradient magnetic separator 40, the wax fraction is hydrocracked using hydrogen in the hydrocracking apparatus 50, thereby reducing the number of carbons of the wax fraction. That is, in the hydrocracking reaction, the hydrocarbon C-C bond is cleaved by the catalyst to produce low-molecular-weight hydrocarbons having a small number of carbons. The liquid hydrocarbons hydrocracked in the hydrocracking apparatus 50 for the wax fraction is brought to a second fractionator 60.

[0026] Even though the solid-liquid separator (separator 20) removes the FT synthesis catalyst from the FT synthetic crude oil, residues of the FT synthesis catalyst are concentrated to the wax fraction flowed out from the bottom of the first fractionator 30, thereby causing a problem in which the residues may be accumulated in the hydrocracking apparatus 50. Such accumulation of the residues may cause a trouble upon operating the hydrocracking apparatus 50. Meanwhile, with regard to properties of the iron group metal used as the FT synthesis catalyst, it has been discovered that the iron group metal has a certain magnetic susceptibility, being paramagnetic regardless of whether it is iron or cobalt. Accordingly, removal of the catalyst by way of magnetic separation is very effective. Additionally, since a large amount of the FT synthesis catalyst is already removed by the above-mentioned solid-liquid separator 20, the concentrated magnetic particles contained in the wax fraction is removed in the high gradient magnetic separator 40 at 100°C to 450°C. The step will be described below.

[0027] The high gradient magnetic separator 40 used in the present invention is a magnetic separator that is designed to function in the following way. That is, in the magnetic separator, a ferromagnetic filling material is disposed in an uniform high-magnetic-field space formed by an external electromagnetic coil, and ferromagnetic or paramagnetic particles are captured to the surface of the filling material by a high magnetic-field gradient of 1 to 20k Gauss/cm generated around the filling material to separate the particles from the wax fraction, and then, the captured particles are washed. For example, as the high gradient magnetic separator, a commercially-supplied device known as the trademark “FEROSEP” and the like may be used.

[0028] With regard to the ferromagnetic filling material, a ferromagnetic fine-wire assembly such as steel net or steel wool having a diameter of 1 μm to 1,000 μm in general, expanded metal, and a conchoidal metallic fine piece may be used. With regard to a type of the metal, use of stainless steel having excellent corrosion resistance, heat resistance, and strength is preferable.

[0029] Furthermore, use of the ferromagnetic metal piece as proposed in Japanese Unexamined Patent Application, First Publication No. H07-70568 is also preferable, where the ferromagnetic metal piece is formed into a plate having two planes; the area of larger plane is equal to an area of a circle having a diameter R of 0.5 mm to 4 mm; the ratio of R to a maximum thickness d of the plate (R/d) is within a range of 5 to 20; and the plate is made of a Fe-Cr-based alloy that contains a main component of Fe, and 5-25 wt% of Cr, 0.5-2 wt% of Si, and 2 wt% or less of C.

[0030] With regard to the step of separating the magnetic particle from the wax fraction in the high gradient magnetic separator 40, the wax fraction is introduced into the magnetic-field space inside the high gradient magnetic separator 40, and the magnetic particles are captured to the ferromagnetic filling material disposed in the magnetic-field space to remove the magnetic particles from the wax fraction. Then, with regard to the step of washing and removing the magnetic particles captured to the filling material, since an amount of the magnetic particles captured by a certain surface area of the filling material is limited, the captured magnetic particles are removed from the filling material by washing when the captured amount reaches a certain amount or the limit amount thereof. The washing and removing step may be carried out in such a manner that the magnetic field is terminated to release the magnetic particles from the filling material, and the magnetic particles are discharged to the outside of the magnetic separator by use of washing liquid. Conditions in the magnetic separation of magnetic particles contained in the wax fraction, and conditions for washing and removing the magnetic particles captured (e.g. adhered) onto the filling material will be described below.

[0031] With regard to conditions for the magnetic separation in the high gradient magnetic separator 40, the field intensity may be suitably selected depending on the liquid residence time described below, and is not particularly limited. However, the magnetic field intensity is preferably 1,500 Gauss or more, more preferably 8,000 Gauss or more, still
more preferably 20,000 Gauss or more, and most preferably 40,000 Gauss or more. This is because the liquid residence time can be shortened whereby the separation can be quickly and efficiently conducted. It is preferable that the upper limit of the magnetic field intensity is as high as possible. However, the output of approximately 500,000 Gauss may be the limit in general.

In the present invention, it is required for the temperature of the liquid in the separator (process temperature) to be 100°C to 450°C. The process temperature is preferably 100°C to 400°C, more preferably 100°C to 300°C, and still more preferably 100°C to 200°C.

The liquid residence time (residence time) may be set depending on the magnetic field intensity, and is not particularly limited. For example, the liquid residence time may be set to three seconds or more, preferably ten seconds or more, and more preferably fifty seconds or more. Additionally, the upper limit of the liquid residence time may be set to a time when an objective removal rate (% by mass) of the magnetic particles is achieved. In general, the upper limit of the liquid residence time may be set to, for example, approximately five minutes.

In addition, in the present invention, the "liquid residence time" refers to a time obtained by dividing the volume of a filling vessel (which the magnetic field is applied to) by the inflow rate of the liquid (e.g. the wax fraction containing magnetic particles) which is introduced into the filling vessel. The liquid residence time can be represented by the following formula.

The liquid residence time (second) = the volume of a filling vessel which the magnetic field is applied to (L) / the inflow rate of the wax fraction containing magnetic particles (L/second).

Next, when operation of the magnetic separation of the magnetic particles is continuously carried out, the removal rate decreases as the amount of the magnetic particles captured by the filling material increases. Therefore, in order to maintain a sufficient removal rate, it is required to carry out the washing and removing step where the captured magnetic particles are discharged to the outside of the magnetic separator after the oil flows through the filling vessel for a predetermined time. In industrial operation, the raw oil fraction containing the magnetic particle may bypass the high gradient magnetic separator 40 during the washing and removing step. However, if the washing operation requires a longer time, a large amount of the magnetic particle flows into the hydrogenation apparatus, and the removal rate decreases. Therefore, an extra separator (not shown) (i.e. the inflow of the raw oil fraction can be switched to the extra separator during the washing operation) may be provided if necessary.

In the washing and removing step of the present invention, the processed oil obtained after the magnetic separation process or the wax cracked produced oil subjected to the hydocracking process after the magnetic separation process may be used as the washing liquid.

The washing and removing step of the present invention can be carried out in the following way. That is, the magnetic field generated around the filling material is eliminated (i.e. the current supply to the magnetic-separation electromagnetic coil is terminated), and the washing liquid is introduced to the bottom of the separator to wash the magnetic particles captured to the filling material. With regard to conditions for washing, the washing-liquid linear velocity may be in a range of 1 cm/sec to 10 cm/sec and preferably in a range of 2 cm/sec to 6 cm/sec.

Hereinafter, the magnetic separation step will be described in more detail with reference to FIG. 2.

FIG. 2 is a schematic view showing the high gradient magnetic separator 40 used in the present invention. The high gradient magnetic separator 40 where the separation is conducted is formed into a vertical filling tower, and is filled with the ferromagnetic filling material. A filling vessel 41 filled with the filling material is magnetized by the magnetic flux formed with an electromagnetic coil 42 which is disposed outside the vertical filling tower, thereby forming a "high gradient magnetic separation space". The space corresponds to the uniform high-magnetic-field space formed by the external electromagnetic coil. The wax fraction heated to a temperature suitable for the operation passes through the separation area from the downside (from the line 31) to the upside at a predetermined flow rate (preferably, at a flow rate where the liquid residence time is within the above-described range), and the magnetic particles are captured to the surface of the filling material during the passage of the wax fraction whereby the magnetic particles are removed therefrom.

While the wax fraction passes through the magnetic separator 40 from the line 31, the washing liquid can bypass via a bypass line for the washing liquid (not shown). When the washing liquid is supplied from a line 43 to wash the magnetic separator 40, the wax fraction can bypass via a bypass line for the wax fraction (not shown) to be directly transferred to the hydocracking apparatus 50 during the washing step. The washing liquid after washing the magnetic separator 40 may be discharged to the outside of the system via a line 44. In such a manner, it is possible to carry out switching between the removing operation and the washing operation, and the alternative and continuous operation. The washing and removing step can be carried out, for example, based on the method disclosed in Japanese Unexamined Patent Application, First Publication No. H06-200260.
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Examples of the hydrocracking catalyst include a carrier of a solid acid onto which an active metal belonging to Group VIII in the periodic table is loaded.

Preferable examples of such a carrier include a carrier containing a crystalline zeolite such as ultra-stable Y (USY) zeolite, HY zeolite, mordenite, or β-zeolite one; and at least one solid acid selected from amorphous metal oxides having heat resistance, such as silica alumina, silica zirconia or alumina boria. Moreover, it is preferable that the carrier be a carrier containing USY zeolite; and at least one solid acid selected from silica alumina, alumina boria, and silica zirconia. Furthermore, a carrier containing USY zeolite and silica alumina is more preferable.

USY zeolite is a Y-type zeolite that is ultra-stabilized by way of a hydrothermal treatment and/or acid treatment, and fine pores within a range of 20 Å to 100 Å are formed in addition to a micro porous structure, which is called micro pores of 20 Å or less originally included in Y-type zeolite. When USY zeolite is used for the carrier of the hydrocracking catalyst, its average particle diameter is not particularly limited. However, the average particle diameter thereof is preferably 1.0 μm or less, or preferably 0.5 μm or less. In USY zeolite, a molar ratio of silica/alumina (i.e. molar ratio of silica to alumina; hereinafter referred to as "silica/alumina ratio") is preferably within a range of 10 to 200, more preferably within a range of 15 to 100, and the most preferably within a range of 20 to 60.

It is preferable that the carrier include 0.1% to 80% by mass of a crystalline zeolite and 0.1% to 60% by mass of a heat-resistant amorphous metal oxide.

A mixture including the above-mentioned solid acid and a binder may be subjected to moulding, and the moulded mixture may be calcined to produce the catalyst carrier. The blend ratio of the solid acid therein is preferably within a range of 1% to 70% by mass, or more preferably within a range of 2% to 60% by mass with respect to the total amount of the carrier. If the carrier includes USY zeolite, the blend ratio of USY zeolite is preferably within a range of 0.1% to 10% by mass, or more preferably within a range of 0.5% to 5% by mass to the total amount of the carrier. If the carrier includes USY zeolite and alumina-boria, the mixing ratio of USY zeolite to alumina-boria (USY zeolite/alumina-boria) is preferably within a range of 0.03 to 1 based on a mass ratio. If the carrier includes USY zeolite and silica alumina, the mixing ratio of USY zeolite to silica alumina (USY zeolite/silica alumina) is preferably within a range of 0.03 to 1 based on a mass ratio.

The binder is not particularly limited. However, the binder is preferably alumina, silica, silica alumina, titania, or magnesia, and is more preferably alumina.

The blend ratio of the binder is preferably within a range of 20% to 98% by mass, or more preferably within a range of 30% to 96% by mass based on the total amount of the carrier.

The calcination temperature of the mixture is preferably within a range of 400°C to 550°C, more preferably within a range of 470°C to 530°C, or particularly preferably within a range of 490°C to 530°C.

Examples of the group VIII metal include cobalt, nickel, rhodium, palladium, iridium, platinum and the like. In particular, metal selected from nickel, palladium and platinum is preferably used singularly or in combination of two or more kinds.

These kinds of metal may be loaded on the above-mentioned carrier according to a common method such as impregnation, ion exchange or the like. The total amount of the loaded metal is not particularly limited. However, the amount of the loaded metal is preferably within a range of 0.1% to 3.0% by mass with respect to the carrier.

Hydrocracking the wax fraction may be performed under the following reaction conditions. That is, the hydrogen partial pressure may be within a range of 0.5 MPa to 12 MPa, or preferably within a range of 1.0 MPa to 5.0 MPa. Liquid hourly space velocity (LHSV) of the wax fraction may be within a range of 0.1 h⁻¹ to 10.0 h⁻¹, or preferably within a range of 0.3 h⁻¹ to 3.5 h⁻¹. The hydrogen/oil ratio is not particularly limited, but may be within a range of 50 NL/L to 1000 NL/L, preferably within a range of 70 NL/L to 800 NL/L.

Additionally, in the present description, "LHSV (liquid hourly space velocity)" refers to a volume flow rate of feedstock per volume of a catalyst bed filled with catalyst under standard conditions (25°C and 101,325 Pa), and the unit "h⁻¹" represents the reciprocal of hours. "NL" being the unit of hydrogen capacity in the hydrogen/oil ratio represents hydrogen volume (L) under normal conditions (0°C and 101,325 Pa).

The reaction temperature for hydrocracking (weight average bed temperature of a catalyst) may be within a range of 180°C to 400°C, preferably within a range of 200°C to 370°C, more preferably within a range of 250°C to 350°C, particularly preferably 280°C to 350°C. If the reaction temperature for hydrocracking exceeds 400°C, not only may the yield of the middle fraction remarkably decrease, but the product may also be colored, thereby limiting use of the product as a fuel base stock. Accordingly, if such a problem arises, the reaction temperature can be adjusted to the above-mentioned temperature range. If the reaction temperature is less than 180°C, alcohols may be insufficiently removed, and may remain therein. If such a problem arises, the reaction temperature can be adjusted to the above-mentioned temperature range in the same manner.

In the hyrorefining (hydroisomerization) apparatus 52 for the middle fraction, the liquid hydrocarbons (mainly having eleven to twenty carbon atoms) of the middle fraction having a middle boiling range (i.e. liquid hydrocarbons supplied from the middle portion of the first fractionator 30 via the line 32) are hyrorefined (hydroisomerized) by use of
hydrogen. This hydorefining reaction is a reaction in which the liquid hydrocarbons are isomerized or hydrogen is added to unsaturated bonds thereof, thereby saturating the bonds. As a result, the product containing hydorefined hydrocarbons is brought to the second fractionator 60.

<Hydroisomerization of middle fraction>

[0054] A known fixed-bed reactor may be used as the hydroisomerizing apparatus 52. In this embodiment of the present invention, the reactor, which is a fixed-bed reactor, is filled with a predetermined hydroisomerizing catalyst, and the middle fraction obtained in the first fractionator 30 is hydroisomerized. As used herein, the hydroisomerization includes conversion of olefins into paraffins by hydrogen addition and conversion of alcohols into paraffins by dehydroxylation in addition to hydroisomerization of n-paraffins to iso-paraffins.

[0055] Examples of the hydroisomerizing catalyst include a carrier of a solid acid onto which an active metal belonging to Group VIII in the periodic table is loaded.

[0056] Preferable examples of such a carrier include a carrier containing one or more kinds of solid acids which are selected from amorphous metal oxides having heat resistance, such as silica alumina, silica zirconium oxide, or alumina-boria.

[0057] A mixture including the above-mentioned solid acid and a binder may be subjected to moulding, and the moulded mixture may be calcined to produce the catalyst carrier. The blend ratio of the solid acid therein is preferably within a range of 1% to 70% by mass, or more preferably within a range of 2% to 60% by mass with respect to the total amount of the carrier.

[0058] The binder is not particularly limited. However, the binder is preferably alumina, silica, silica alumina, titania, or magnesia, and is more preferably alumina. The blend ratio of the binder is preferably within a range of 30% to 99% by mass, or more preferably within a range of 40% to 98% by mass based on the total amount of the carrier.

[0059] The calcination temperature of the mixture is preferably within a range of 400°C to 550°C, more preferably within a range of 470°C to 530°C, or particularly preferably within a range of 490°C to 530°C.

[0060] Examples of the group VIII metal include cobalt, nickel, rhodium, palladium, iridium, platinum and the like. In particular, metal selected from nickel, palladium and platinum is preferably used singularly or in combination of two or more kinds.

[0061] These kinds of metal may be loaded on the above-mentioned carrier according to a common method such as impregnation, ion exchange or the like. The total amount of the loaded metal is not particularly limited. However, the amount of the loaded metal is preferably within a range of 0.1% to 3.0% by mass with respect to the carrier.

[0062] The hydroisomerization of the middle fraction may be performed under the following reaction conditions. The hydrogen partial pressure may be within a range of 0.5 MPa to 12 MPa, preferably within a range of 1.0 MPa to 5.0 MPa. Liquid hourly space velocity (LHSV) of the middle fraction may be within a range of 0.1 h⁻¹ to 10.0 h⁻¹, or preferably within a range of 0.3 h⁻¹ to 3.5 h⁻¹. The hydrogen/oil ratio is not particularly limited. However, the hydrogen/oil ratio may be within a range of 50 NL/L to 1000 NL/L, or preferably within a range of 70 NL/L to 800 NL/L.

[0063] The reaction temperature for the hydroisomerization may be within a range of 180°C to 400°C, preferably within a range of 200°C to 370°C, more preferably within a range of 250°C to 350°C, or particularly within a range of 280°C to 350°C. If the reaction temperature exceeds 400°C, a side reaction wherein the middle fraction is decomposed into a light fraction may be promoted, whereby yield of the middle fraction will be lowered, but also the product may be colored, and use of the middle fraction as a fuel base stock may be limited. Accordingly, if such a problem arises, the reaction temperature can be adjusted to the above-mentioned temperature range. On the other hand, if the reaction temperature is less than 180°C, alcohols may be insufficiently removed, and remain therein. If such a problem arises, the reaction temperature can be adjusted to the above-mentioned temperature range in the same manner.

[0064] The hydrotreating apparatus 54 for the naphtha fraction hydrotreats the naphtha fraction (mainly having ten or less carbon numbers) flowed out from the top of the first fractionator 30 by use of hydrogen gas. As a result, the product containing the hydrotreated hydrocarbons is brought to a stabilizer 70 for the naphtha fraction, and the refined naphtha fraction can be obtained via a line 71 connected to the bottom thereof. On the other hand, gas mainly containing hydrocarbons having four or less carbon atoms is discharged from the top of the stabilizer 70 for the naphtha fraction via a line 72.

[0065] Subsequently, the hydrocarbons treated in the hydrocracking apparatus 50 for the wax fraction are combined with hydrocarbons treated in the hydroisomerizing apparatus 52 for the middle fraction as described above, the combined hydrocarbons are refined in the second fractionator 60. Consequently, a kerosene fraction (having a boiling point in the range of from approximately 150°C to approximately 250°C) is extracted via a line 63, and a gas oil fraction (having a boiling point in the range of from approximately 250°C to approximately 350°C) is extracted via a line 62. Each fraction may be stored suitably in a storage tank (not shown). The method of mixing the hydrocarbons treated in the hydrocracking apparatus 50 for the wax fraction and the hydrocarbons treated in the hydroisomerizing apparatus 52 for the middle fraction is not particularly limited. Tank blending or line blending may be selected. Then, a light fraction extracted from
the top of the second fractionator 60 is introduced into the stabilizer 70 via a line 55.

[0066] A bottom fraction flowed out from the bottom of the second fractionator 60 is recycled suitably to the inlet of the hydrocracking apparatus 50 for the wax fraction via a line 61 so as to be subjected to the hydrocracking process again, thereby improving the yield of the hydrocracked product.

[0067] In the above-described manner, the naphtha fraction, the kerosene fraction, and the gas oil fraction can be produced from the FT synthetic crude oil. Furthermore, since the wax fraction inevitably contained in the FT synthetic crude oil is efficiently cracked whereby the wax fraction can be converted to the lighter fraction, the yield can be remarkably improved.

EXAMPLES

[0068] Hereinafter, the present invention will be described in more detail with reference to Examples. However, the present invention is not limited to Examples.

<Preparation of catalyst>

(Catalyst A)

[0069] Silica alumina (molar ratio of silica/alumina : 14), and an alumina binder were mixed and kneaded at a weight ratio of 60 : 40, and the mixture was moulded into a cylindrical form having a diameter of approximately 1.6 mm and a length of approximately 4 mm. Then, this was calcined at 500°C for one hour, thereby producing a carrier. The carrier was impregnated with a chloroplatinic acid aqueous solution to distribute platinum on the carrier. The impregnated carrier was dried at 120°C for three hours, and then, calcined at 500°C for one hour, thereby producing catalyst A. The amount of platinum loaded on the carrier was 0.8% by mass to the total amount of the carrier.

(Catalyst B)

[0070] USY zeolite (molar ratio of silica/alumina : 37) having an average particle diameter of 1.1 μm, silica alumina (molar ratio of silica/alumina : 14) and an alumina binder were mixed and kneaded at a weight ratio of 3 : 57 : 40, and the mixture was moulded into a cylindrical form having a diameter of approximately 1.6 mm and a length of approximately 4 mm. Then, this was calcined at 500°C for one hour, thereby producing a carrier. The carrier was impregnated with a chloroplatinic acid aqueous solution to distribute platinum on the carrier. The impregnated carrier was dried at 120°C for three hours, and then, calcined at 500°C for one hour, thereby producing catalyst B. The amount of platinum loaded on the carrier was 0.8% by mass to the total amount of the carrier.

[Example 1]

<Method of producing synthetic fuel>

(Fractionation of FT synthetic crude oil)

[0071] In FIG. 1, the produced oil (FT synthetic crude oil) (the content of hydrocarbons having a boiling point of approximately 150°C or more was 84% by mass, the content of hydrocarbons having a boiling point of approximately 360°C or more was 42% by mass where the contents were based on the total amount of the FT synthetic crude oil (the sum of hydrocarbons having five or more carbon atoms)) obtained in the FT synthesis reactor 10, which was a bubble column reactor, was extracted via the line 3. Subsequently, the remaining catalyst was removed with the solid-liquid separator 20 using a filter according to a conventional method. Since the type of the reactor was a bubble column reactor in which cobalt-based catalyst particles freely flowed in the liquid medium, very fine catalyst particles form remained therein. Although the remaining catalyst was not completely removed, the remaining catalyst was removed to a level at which the content of the remaining catalyst did not cause a trouble in the subsequent processes.

[0072] Subsequently, in the first fractionator 30, the FT synthetic crude oil, from which the remaining catalyst was removed, was fractionated into three fractions, e.g. the naphtha fraction having a boiling point of approximately 150°C, the middle fraction having a boiling point in the range of from approximately 150°C to approximately 350°C, and the wax fraction of the bottom fraction.

The wax fraction extracted from the bottom of the first fractionator 30 contained impurities. That is, the wax fraction contained 20 mass ppm of the Fischer-Tropsch synthesis catalyst (FT catalyst: the cobalt loading amount was 30% by mass (with respect to the catalyst), and an average particle diameter was 10 μm) based on the total amount of the wax fraction.
The catalyst A (150 ml) was filled into the hydroisomerizing apparatus 52 which was a fixed-bed reactor. Then, the middle fraction obtained from the first fractionator 30 via the line 32 was supplied to the top of the hydroisomerizing reaction tower (hydroisomerizing apparatus) 52 at a feed rate of 225 ml/h. In a hydrogen stream, the hydrogenation process was carried out in reaction conditions described in Table 1. That is, hydrogen was supplied to the top of the hydroisomerizing reactor 52 at the hydrogen/oil ratio of 338 NL/L with respect to the middle fraction, and the back pressure value was adjusted so that the inlet pressure of the hydroisomerizing reactor 52 was constantly maintained at 3.0 MPa. In such conditions, the hydroisomerizing reaction was carried out. The reaction temperature was 308°C.

The electromagnetic-type high gradient magnetic separator (FEROSEP (trademark)) 40 having a structure shown in FIG. 2 was disposed between the first fractionator 30 and the hydrocracking apparatus 50. The wax fraction obtained from the bottom of the first fractionator 30 via the line 31 was processed under conditions shown in Table 2 to remove the magnetic particles. The magnetic particle removal rate is also shown in Table 2.

The magnetic particle removal rate refers to a value calculated by the following equation based on the magnetic particle density at the inlet of the magnetic separator obtained from the measurement results obtained using a laser diffraction particle size analyzer (SALD-3100) manufactured by SHIMADZU Corporation (hereinafter, the same applies).

\[
\text{The magnetic particle removal rate (\% by mass)} = 100 \times \left( \frac{\text{the magnetic particle density at the inlet of the magnetic separator} - \text{the magnetic particle density at the outlet of the magnetic separator}}{\text{the magnetic particle density at the inlet of the magnetic separator}} \right)
\]

The catalyst B (150 ml) is filled into the fixed-bed reactor of the hydrocracking apparatus 50. Subsequently, the wax fraction from which the magnetic particle was removed by the electromagnetic-type high gradient magnetic separator (FEROSEP (trademark)) 40 was supplied to the top of the hydrocracking apparatus 50 at a feed rate of 300 ml/h. In a hydrogen stream, the hydrocracking process was carried out in the reaction conditions described in Table 1. That is, hydrogen was supplied to the top of the reactor 60 at the hydrogen/oil ratio of 676 NL/L with respect to the wax fraction after the magnetic particles were removed, and the back pressure value was adjusted so that the inlet pressure of the hydrocracking apparatus was constantly maintained at 4.0 MPa. In such conditions, the hydrocracking reaction was carried out. The reaction temperature was 329°C.

The hydroisomerized product of the middle fraction (hydroisomerized middle fraction) and the hydrocracked product (cracked wax fraction) of the wax fraction obtained as described above were blended in the line (i.e. line blending). The mixture was introduced into the second fractionator 60, and was fractionated therein. Subsequently, the diesel fuel base stock was extracted therefrom and was stored in a tank (not shown).

Additionally, the top component in the second fractionator 60 was continuously recycled to the inlet of the hydrocracking apparatus 50 via the line 61, and the recycled component was hydrocracked again.

The bottom component in the second fractionator 60 was continuously recycled to the inlet of the hydrocracking apparatus 50 via the line 61, and the recycled component was hydrocracked again.

The Synthetic Fuel was produced in the same manner as Example 1 except that the treatment to the wax fraction using the magnetic separator was not performed.

(Examples 2 to 6)

The treatment with the magnetic separator was carried out with respect to the wax fraction to produce the synthetic fuel in the same manner as Example 1 except for the magnetic field intensity and the liquid residence time. The magnetic particle removal rate is shown in Table 2.

(Comparative Example 1)
(Comparative Example 2)

[0081] The synthetic fuel was produced in the same manner as Example 1 except that the temperature in the treatment using the magnetic separation was set to 80°C.

(Comparative Example 3)

[0082] The synthetic fuel was produced in the same manner as Example 1 except that the temperature in the treatment using the magnetic separation was set to 500°C.

(Result)

[0083] In the Examples 1 to 6 in which the electromagnetic high gradient magnetic separator was installed between the first fractionator and the hydrocracking apparatus whereby the magnetic particles were removed in the range of treatment temperature of 100°C to 450°C, reduction of the magnetic particles having an adverse influence on the hydrocracking process could be achieved. In particular, when the treatment was carried out in conditions where the magnetic field intensity was 10,000 Gauss or more and the liquid residence time was fifteen seconds or more, the magnetic particles could be remarkably reduced.

[0084] On the other hand, in the Comparative Example 2 where the treatment temperature was set to 80°C, the treatment of removing the magnetic particles could not be carried out because the wax fraction was coagulated inside the magnetic separator. Additionally, in the Comparative Example 3 where the treatment temperature was set to 500°C, it was impossible to continuously carry out the normal operation due to decomposition or polymerization of the wax fraction.
<table>
<thead>
<tr>
<th></th>
<th>EXAMPLE 1</th>
<th>EXAMPLE 2</th>
<th>EXAMPLE 3</th>
<th>EXAMPLE 4</th>
<th>EXAMPLE 5</th>
<th>EXAMPLE 6</th>
<th>COMPARATIVE EXAMPLE 1</th>
<th>COMPARATIVE EXAMPLE 2</th>
<th>COMPARATIVE EXAMPLE 3</th>
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</thead>
<tbody>
<tr>
<td><strong>CATALYST</strong></td>
<td>CATALYST A</td>
<td>←</td>
<td>←</td>
<td>←</td>
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<td>←</td>
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<td><strong>LHSV h⁻¹</strong></td>
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<td>←</td>
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<td>←</td>
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<td><strong>HYDROGEN/OIL RATIO N L/L</strong></td>
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<td>←</td>
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<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
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<tr>
<td><strong>CATALYST</strong></td>
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<td>←</td>
<td>←</td>
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<td><strong>REACTION TEMPERATURE °C</strong></td>
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</table>
The present invention is applicable to production of the fuel oil from the FT synthetic crude oil obtained by the FT synthesis method using carbon monoxide and hydrogen as raw materials. Accordingly, the present invention has high applicability in industries including GTL (Gas to Liquids) and petroleum refinery.

Claims

1. A method of producing synthetic fuel from Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method, the method comprising the steps of:

   (a) fractionating, in a fractionator, Fischer-Tropsch synthetic crude oil obtained by a Fischer-Tropsch synthesis method into at least two fractions of a middle fraction containing a component having a boiling range corresponding to diesel fuel oil, and a wax fraction containing a wax component heavier than the middle fraction;

   (b) separating and removing a magnetic particle contained in the wax fraction obtained in the step (a) at 100°C to 450°C by using a high gradient magnetic separator; and

   (c) hydrocracking the wax fraction obtained in the step (b) from which the magnetic particle is separated and removed.

2. The method of producing synthetic fuel according to Claim 1, wherein, in the step (b), a ferromagnetic filling material is disposed in a space where a magnetic field is generated inside the high gradient magnetic separator, the wax fraction obtained in the step (a) is introduced into the magnetic field space in the state where the magnetic field is generated to capture the magnetic particle to the ferromagnetic filling material, and then washing liquid is introduced into the space where the ferromagnetic filling material is disposed while eliminating the magnetic field to discharge the magnetic particle to the outside of the high gradient magnetic separator.

3. The method of producing synthetic fuel according to Claim 1 or 2, wherein, in the step (b) of separating and removing the magnetic particle using the high gradient magnetic separator is carried out in conditions where the magnetic field intensity is 1,500 Gauss or more and the liquid residence time is three seconds or more.

INDUSTRIAL APPLICABILITY

The present invention is applicable to production of the fuel oil from the FT synthetic crude oil obtained by the FT synthesis method using carbon monoxide and hydrogen as raw materials. Accordingly, the present invention has high applicability in industries including GTL (Gas to Liquids) and petroleum refinery.

Table 2

<table>
<thead>
<tr>
<th>Magnetic Field Intensity (Gauss)</th>
<th>Treatment Temperature (°C)</th>
<th>Liquid Residence Time (Seconds)</th>
<th>Magnetic Particle Removal Rate (mass%)</th>
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<tbody>
<tr>
<td>EXAMPLE 1</td>
<td>50000</td>
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<td>15</td>
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<td>EXAMPLE 2</td>
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<td>150</td>
<td>60</td>
</tr>
<tr>
<td>EXAMPLE 3</td>
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<td>150</td>
<td>100</td>
</tr>
<tr>
<td>EXAMPLE 4</td>
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<td>EXAMPLE 5</td>
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</tr>
<tr>
<td>COMPARATIVE EXAMPLE 1</td>
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<tr>
<td>COMPARATIVE EXAMPLE 2</td>
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</tr>
<tr>
<td>COMPARATIVE EXAMPLE 3</td>
<td>50000</td>
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**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**
C10G32/02 (2006.01)i, C10G2/00 (2006.01)i, C10G47/00 (2006.01)i, C10G67/02 (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)
C10G1/00-99/00

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>JP 2007-527450 A (Chevron USA Inc.), 27 September, 2007 (27.09.07), Claims, Par. Nos. [0021], [0022], [0026] to [0028], Fig. 1 &amp; US 2005/004414 A1 &amp; GB 2420789 A &amp; WO 2005/002701 A2 &amp; NL 1026567 C &amp; NL 1026567 A1</td>
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<td>Y</td>
<td>US 4605678 A (J.A.Brennan et al.), 12 August, 1986 (12.08.86), Claim 1; column 4, line 59 to column 5, line 26; column 5, lines 54 to 68; column 10, line 55 to column 11, line 7 (Family: none)</td>
<td>1-3</td>
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[X] 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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  ‘&’ document member of the same patent family

Date of the actual completion of the international search 21 May, 2009 (21.05.09)

Date of mailing of the international search report 02 June, 2009 (02.06.09)

Name and mailing address of the ISA/ Japanese Patent Office

Authorized officer

Facsimile No. Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)
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Patent documents cited in the description

- JP H0770568 B [0029]
- JP H06200260 B [0039]