



(11)

EP 4 458 928 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

06.11.2024 Bulletin 2024/45

(51) International Patent Classification (IPC):

C10G 65/02 (2006.01) **C10G 45/02** (2006.01)
C10G 45/44 (2006.01)

(21) Application number: **22918460.1**

(52) Cooperative Patent Classification (CPC):

C10G 45/02; C10G 45/44; C10G 65/02

(22) Date of filing: **28.12.2022**

(86) International application number:

PCT/CN2022/142685

(87) International publication number:

WO 2023/131019 (13.07.2023 Gazette 2023/28)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA

Designated Validation States:

KH MA MD TN

(30) Priority: **06.01.2022 CN 202210008433**

06.01.2022 CN 202210008420

06.01.2022 CN 202210014492

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(54) **HYDROGENATION METHOD AND HYDROGENATION SYSTEM FOR HYDROCARBON OIL**

(57) The present invention relates to the field of oil refining and chemical engineering, and disclosed are a hydrogenation method and a hydrogenation system for a hydrocarbon oil. The method comprises the following steps: (1) in the presence of hydrogen, subjecting a hydrocarbon oil raw material to a gas-phase desulfurization reaction in a gas-phase desulfurization reactor to obtain a gas-phase desulfurization reaction product; (2) pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow; and (3) feeding the pressurized material flow into a liquid phase hydrogenation reactor, and subjecting liquid phase components in the pressurized material flow to liquid-phase hydrogenation reaction in a liquid-phase hydrogenation reactor to obtain a liquid-phase hydrogenation reaction product. The method and the system provided in the present invention can achieve a deep hydrogenation effect, and can also simplify the technological process, reduce the

reaction severity and improve the chemical reaction efficiency on the whole.

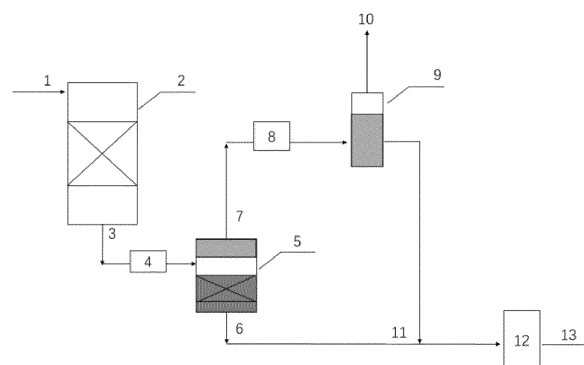


FIG. 1

EP 4 458 928 A1

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of the Chinese patent application No. "202210008433.6", the Chinese patent application No. "202210008420.9", and the Chinese patent application No. "202210014492.4", filed on January 6, 2022, the contents of which are specifically and entirely incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to the field of oil refining and chemical engineering, in particular to a hydrogen method and a hydrogen system for hydrocarbon oil.

BACKGROUND ART

[0003] The emissions formed by the combustion of sulfur and polycyclic aromatic hydrocarbons in diesel oil will pollute the atmospheric environment that mankind relies on for existence, as a result, the upgrading pace of diesel oil quality standards has been continuously accelerated in various countries in the world. The emission standard V of diesel oil in China implemented in 2017 required that the sulfur content shall not be higher than 10 mg/kg, the quality standard VI of diesel oil in China stipulated in 2019 required that the content of polycyclic aromatic hydrocarbons shall not be higher than 11%, and the quality standard VIB of diesel oil in China implemented since 2023 imposed a stringent requirement that the content of polycyclic aromatic hydrocarbons shall not be higher than 5%. Meanwhile, the market demand for processing secondary raw materials in China has been gradually increasing, the content of aromatic hydrocarbons in the inferior raw materials (e.g., catalytic diesel oil) is up to 60%, which imposes higher requirements on the activity of the catalysts. However, from the perspective of the reaction mechanism of deep desulfurization and deep dearomatization, there is a large difference between the requirements of deep desulfurization and deep dearomatization in the reaction environment. In terms of desulfurization reaction, the removal of small molecule sulfur mainly follows a direct desulfurization route, i.e., hydrogenolysis desulfurization. The macromolecular sulfide with a lower reaction activity follows the hydrodesulfurization reaction route, namely, hydrogenation is carried out on the aromatic ring, and then hydrogenolysis desulfurization is carried out. Therefore, the hydrogenolysis (endothermic) of small molecule sulfides and hydrogenation (significantly exothermic) of aromatic ring-containing substances primarily occur in the upper portion of the reactor having an environment of relatively low temperature and high hydrogen partial pressure. The accumulation of heat and hydrogen sulfide at the lower part of the reactor causes the reaction environment to be high temperature and low hydrogen partial pressure, the reaction environment is favorable for further hydrogenolysis of the hydrogenated macromolecular sulfide, but is very unfavorable for further saturation of aromatic hydrocarbons due to the severe thermodynamic limitation of aromatic hydrocarbon hydrogenation. Especially, at the final stage of the reaction, the catalyst activity is attenuated, and the dearomatization effect is further affected because there are no better operating means except for raising the temperature. Besides the different requirements of deep desulfurization and deep dearomatization on the reaction environment, the competitive adsorption of the aromatic hydrocarbons on the surface of the catalyst also has an inhibitive effect on deep desulfurization, thus the traditional hydrogenation technology can hardly meet the dual requirements of ultra-deep desulfurization and efficient saturation of the aromatic hydrocarbons, thus the necessity and urgency of upgrading the diesel oil cleaning technology are further highlighted.

[0004] In terms of the prior art, if the deep dearomatization is further carried out based on deep desulfurization, the first solution relates to the method of reducing the hourly volume space velocity of the reaction (i.e., the method of reducing the treatment capacity or increasing the number of reactors) by utilizing the existing catalyst system, but the method is unreasonable from the prospect of economic efficiency. The second solution relates to the adoption of a two-stage technological process, after the conventional hydrogenation process, the generated oil is subjected to stripping to remove hydrogen sulfide and enters a noble metal hydrogenation reactor, the solution will also greatly increase the use cost of catalyst and the process complexity, the technological process is still not an optimal scheme.

[0005] CN108085058B discloses a deeply dearomatization method for hydrocarbon oil. The method adopts mild temperature and pressure conditions, such that the raw oil and hydrogen gas pass through a highly dispersed Pt-Pd/Al₂O₃ catalyst, the gas-phase reaction product is compressed for recycling, and the liquid-phase is a product with a low content of aromatic hydrocarbons, but the Pt-Pd/Al₂O₃ hydrogenation catalyst is mainly suitable for dearomatization of a diesel oil raw material with low sulfur content, its desulfurization and dearomatization effects of the inferior diesel are not satisfactory.

[0006] CN109926067A discloses a platinum-palladium-cobalt ternary metal hydrogenation dearomatization catalyst and a preparation method thereof. The method adopts a reactive metal precursor substep impregnation method so that the utilization rate of platinum palladium noble metal is high, and the synergistic catalyst capability is high; in addition,

platinum palladium is introduced, such that the aromatic hydrogenation performance of non-noble metal cobalt is enhanced. However, the catalyst is still suitable for the hydrocarbon oil from which the sulfur-containing compounds are basically removed, to avoid the influence of hydrogen sulfide on the deep dearomatization of the noble metals, and the catalyst cannot be used for the desulfurization and dearomatization of the inferior diesel.

SUMMARY OF THE INVENTION

[0007] The present invention aims to overcome the defects of the prior art and provides a hydrogen method and a hydrogen system for a hydrocarbon oil, the method and the system provided in the present invention can achieve a deep hydrogenation effect, and can also simplify the technological process, reduce the reaction severity and improve the chemical reaction efficiency on the whole.

[0008] The first aspect of the present invention provides a hydrogenation method of hydrogen oil, the method comprises the following steps:

- (1) subjecting a hydrocarbon oil raw material to a gas-phase desulfurization reaction in a gas-phase hydrogenation reactor in the presence of hydrogen gas to obtain a gas-phase desulfurization reaction product;
- (2) pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;
- (3) feeding the pressurized material flow into a liquid-phase hydrogenation reactor, and subjecting liquid-phase components in the pressurized material flow to liquid-phase hydrogenation reaction in a liquid-phase hydrogenation reactor to obtain a liquid-phase hydrogenation reaction product.

[0009] Preferably, the conditions of the gas-phase desulfurization reaction comprise: the pressure is within a range of 0.1-2.8 MPa, more preferably within a range of 0.5-2 MPa; the temperature is within a range of 260-400°C, more preferably within a range of 320-390°C; the volume ratio of hydrogen/oil is within a range of 100-900, more preferably within a range of 300-700; and the volume space velocity is within a range of 0.5-3 h⁻¹, more preferably within a range of 0.8-2 h⁻¹.

[0010] Preferably, the conditions of the liquid-phase hydrogenation reaction comprise: the pressure is within a range of 2-8 MPa, more preferably within a range of 3-6 MPa; the temperature is within a range of 200-400°C, preferably 260-360°C, and the volume space velocity is within a range of 0.1-3 h⁻¹, more preferably 0.5-1 h⁻¹.

[0011] The second aspect of the present invention provides a hydrogenation system of a hydrocarbon oil, the system comprises a gas-phase hydrogenation reactor, a pressurizing device, and a liquid-phase hydrogenation reactor connected in sequence, wherein the gas-phase hydrogenation reactor is filled with a first hydrogenation catalyst, and the liquid-phase hydrogenation reactor is filled with a second hydrogenation catalyst;

the gas-phase hydrogenation reactor is used for carrying out a gas-phase desulfurization reaction of the hydrocarbon oil raw material and hydrogen gas to obtain a gas-phase desulfurization reaction product;

the pressurizing device is used for pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;

the liquid-phase hydrogenation reactor is used for contacting the pressurized material flow with the second hydrogenation catalyst to perform a liquid-phase hydrogenation reaction to obtain a liquid-phase hydrogenation reaction product.

[0012] Compared with the prior art, the hydrogenation method and system of the present invention have the following advantages:

(1) The hydrogenation method and system of the present invention can remove the small molecules which are easily reactive from the gas-phase hydrogenation reactor, the unreacted large molecules only need to be liquefied by small-amplitude pressurization and enter the liquid-phase hydrogenation reactor, such that the heavy components which can be easily liquefied are subjected to a deep hydrorefining reaction, thereby avoiding the defects in the prior art that deep desulfurization and dearomatization are performed in the same reaction system and the reaction conditions are difficult to be compatible. The present inventors have discovered in research that competitive adsorption of other substances (e.g., aromatic hydrocarbon substances) in the hydrocarbon oil can be greatly reduced by carrying out gas-phase hydrosulfurization on the hydrocarbon oil, it is conducive to the targeted desulfurization reaction, in addition, through synergy with a liquid-phase hydrogenation reactor, the hydrogenation method and system is more suitable for the subsequent dearomatization and the deep removal of other substances in the hydrocarbon oil.

(2) The hydrogenation method and system of the present invention promote synchronous liquefaction of hydrogen and petroleum products by pressurizing the gas-phase desulfurization reaction product and avoid the influence of

hydrogen sulfide on the activity of a catalyst when the hydrogen and hydrogen sulfide enter a subsequent liquid-phase hydrogenation reactor due to the different dissolution laws of hydrogen and hydrogen sulfide in the petroleum products, so that the inhibition effect of hydrogen sulfide on deep desulfurization in the traditional liquid-phase hydrogenation technology can be desirably avoided, and the arrangement of steam stripping and hydrogen sulfide removal device between two reactors is also saved.

(3) The present invention can realize the hydrorefining of hydrocarbon oil under the more mild operating conditions and a more simplified technological process, such as deep desulfurization and dearomatization by taking poor-quality diesel as the raw material. Among the gas-phase desulfurization reaction product, the reacted small molecules are not liquefied in the pressurizing process and are liquefied only through a heat exchanger and high-pressure separation, such a liquefying means is favorable for separating hydrogen from raw materials, and can recover a large amount of hydrogen for recycling and improve the utilization rate of the hydrogen. The hydrogenated light component separated under high pressure can mix with the hydrogenated heavy component and then enter a subsequent stream stripping and fractionation system. The whole reaction system does not need a hydrogen compressor in a fixed-bed reaction system and a circulating oil pump in a liquid-phase hydrogenation reaction system, thereby decreasing the investment cost, simplifying the technological process, improving the reaction efficiency, and reducing the reaction severity.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

FIG. 1 illustrates a schematic diagram of a hydrogenation method and system of hydrogen oil according to a specific embodiment provided by the present invention;

FIG. 2 illustrates a schematic diagram of a hydrogenation method and system of a hydrocarbon oil according to another specific embodiment provided by the present invention.

DESCRIPTION OF REFERENCE SIGNS

[0014] As shown in FIG. 1, the reference sign 1 denotes a diesel feedstock and hydrogen; 2 denotes a gas-phase hydrogenation reactor; 3 denotes a gas-phase desulfurization reaction product; 4 denotes a pressurizing device; 5 denotes a liquid-phase hydrogenation reactor; 6 denotes a liquid-phase hydrogenation reaction product; 7 denotes a gas-phase component; 8 denotes a heat exchanger; 9 denotes a high-pressure separation device; 10 denotes a hydrogen containing hydrogen sulfide; 11 denotes a hydrogenated light component; 12 denotes a stream stripping and fractionation device; 13 denotes a refined diesel product.

[0015] As shown in FIG. 2, the reference sign 1 denotes a wax oil feedstock and hydrogen; 2 denotes a gas-phase hydrogenation reactor; 3 denotes a gas-phase desulfurization reaction product; 4 denotes a pressurizing device; 5 denotes a liquid-phase hydrogenation reactor; 6 denotes a liquid-phase hydrogenation reaction product; 7 denotes a gas-phase component; 8 denotes a heat exchanger; 9 denotes a high-pressure separation device; 10 denotes a hydrogenated light component; 11 denotes a hydrogen containing hydrogen sulfide; 12 denotes a third hydrogenation reactor; 13 denotes a special petroleum product.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] The terminals and any value of the ranges disclosed herein are not limited to the precise ranges or values, such ranges or values shall be comprehended as comprising the values adjacent to the ranges or values. As for numerical ranges, the endpoint values of the various ranges, the endpoint values and the individual point values of the various ranges, and the individual point values may be combined with one another to produce one or more new numerical ranges, which should be deemed have been specifically disclosed herein.

[0017] The description of the exemplary embodiments shall be read with reference to the accompanying drawings, which are considered a part of the entire written description. In the specification, the relative terms such as "lower", "upper", "horizontal", "vertical", "above", "below", "up", "down", "top" and "bottom" as well as derivatives thereof (e.g., "horizontally", "downwardly", "upwardly") should be construed to the orientation shown in the then described accompanying drawings. These relative terms serve to facilitate description and do not require that the apparatus is constructed or operated in a particular orientation. Unless otherwise specified, the term "connected" used herein refers to a relationship, wherein the structures are secured or connected either directly or indirectly through an intermediate structure.

[0018] The first aspect of the present invention provides a hydrogenation method of hydrogen oil, the method comprises the following steps:

(1) subjecting a hydrocarbon oil raw material to a gas-phase desulfurization reaction in a gas-phase hydrogenation reactor in the presence of hydrogen gas to obtain a gas-phase desulfurization reaction product;
 (2) pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;
 (3) feeding the pressurized material flow into a liquid-phase hydrogenation reactor, and subjecting liquid-phase components in the pressurized material flow to liquid-phase hydrogenation reaction in a liquid-phase hydrogenation reactor to obtain a liquid-phase hydrogenation reaction product.

[0019] The hydrogen in step (1) of the present invention may be any hydrogen-containing gas capable of providing hydrogen, which may be fresh hydrogen, recycled hydrogen, or hydrogen-rich gas. The hydrogen-containing gas described in the present invention can be clearly understood by those skilled in the art after they understand the technical schemes of the present invention.

[0020] The present invention has a wider selection range on the hydrocarbon oil raw material, and the method provided by the present invention is suitable for any hydrocarbon oil that needs to simultaneously remove small-molecule sulfides and other macromolecular impurities, including but not limited to at least one selected from the group consisting of inferior diesel, aviation kerosene, wax oil, and naphtha. The method provided by the present invention can mainly remove the small molecule sulfides from the gas-phase hydrogenation reactor, the unreacted large molecules only need to be liquefied by small-amplitude pressurization and enter the liquid-phase hydrogenation reactor, such that the heavy components which can be easily liquefied are subjected to a deep hydrotreating reaction.

[0021] The present invention has a wider selection range of the hydrocarbon oil raw material properties, preferably, the inferior diesel has an initial boiling point of 150-200°C, an end boiling point of 320-400°C, S content not higher than 20,000 μg/g, more preferably not higher than 15,000 μg/g, N content not higher than 1,000 μg/g, more preferably not higher than 800 μg/g, and polycyclic aromatic hydrocarbon content not higher than 50 wt%. For example, the S content of the inferior diesel may be exemplified by, but not limited to 8,000 μg/g, 9,000 μg/g, 10,000 μg/g, 11,500 μg/g, etc., and the N content is exemplified by, but not limited to 500 μg/g, 600 μg/g, 700 μg/g, etc., and the polycyclic aromatic hydrocarbon content may be exemplified by, but not limited to 25wt%, 30wt%, 35wt%, 40wt%, 45wt%, etc.

[0022] Preferably, the aviation kerosene has an initial boiling point of 80-150°C, an end boiling point of 200-300°C, S content not higher than 8,000 μg/g, more preferably not higher than 4,000 μg/g, N content not higher than 100 μg/g, more preferably not higher than 20 μg/g. For example, the S content of aviation kerosene may be exemplified by, but not limited to 500 μg/g, 1,000 μg/g, 2,000 μg/g, 3,000 μg/g, etc., and the N content may be exemplified by, but not limited to 5 μg/g, 10 μg/g, 15 μg/g, etc.

[0023] Preferably, the wax oil has an initial boiling point of 160-220°C, an end boiling point of 300-400°C, S content not higher than 30,000 μg/g, more preferably not higher than 20,000 μg/g, N content not higher than 2,000 μg/g, more preferably not higher than 1,500 μg/g, and polycyclic aromatic hydrocarbon content not higher than 60 wt%. For example, the S content of the wax oil may be exemplified by, but not limited to 500 μg/g, 1,000 μg/g, 2,000 μg/g, 5,000 μg/g, 8,000 μg/g, 9,000 μg/g, 10,000 μg/g, 15,000 μg/g, etc., and the N content may be exemplified by, but not limited to 500 μg/g, 700 μg/g, 1,000 μg/g, 1,200 μg/g, etc. The polycyclic aromatic hydrocarbon content can be exemplified by, but not limited to 10wt%, 20wt%, 30wt%, 40wt%, 50wt%, etc.

[0024] In the present invention, the symbol "≥" has a meaning of not higher than, and the symbol "≤" has a meaning of not less than.

[0025] According to a preferred embodiment of the present invention, the gas-phase desulfurization reaction is performed in the presence of a first hydrogenation catalyst, the first hydrogenation catalyst is a catalyst having a hydrodesulfurization function. The present invention has a wider selection range of the catalyst having a hydrodesulfurization function, which can be a conventional choice in the art, for example, the catalyst having a hydrodesulfurization function comprises a carrier and a hydrogenation active metal, wherein the carrier is an inorganic refractory oxide and is generally one or more selected from the group consisting of alumina, amorphous silica-alumina, silica, and titanium oxide; the hydrogenation active metal comprises a VIB group metal component and/or a VIII group metal component. In the catalyst having a hydrodesulfurization function, the VIB group metal component is preferably selected from tungsten and/or molybdenum, the content of the VIB group metal component calculated in terms of oxide by mass in the catalyst is 5-30%, preferably 15-30%; the VIII group metal component is preferably selected from nickel and/or cobalt, and the content of the VIII group metal component calculated in terms of oxide by mass in the catalyst is 1-6%, preferably 2-6%. The catalyst having a hydrodesulfurization function may further comprise an auxiliary component, such as at least one selected from the group consisting of phosphorus, silicon, boron, magnesium, and fluorine, and the mass content of the auxiliary component in the catalyst having a hydrodesulfurization function is generally less than 6 wt%.

[0026] The catalyst having a hydrodesulfurization function may be voluntarily prepared with any method or maybe a commercially available catalyst, for example, at least one of FHUDES-5, FHUDES-6, and FHUDES-7 catalysts researched and developed by the SINOPEC Fushun Research Institute of Petroleum and Petrochemical (FRIPP).

[0027] According to the method provided by the present invention, the conditions of the gas-phase desulfurization reaction preferably comprise: the pressure is within a range of 0.1-2.8 MPa, more preferably within a range of 0.5-2

MPa; the temperature is within a range of 260-400°C, more preferably within a range of 320-390°C; the volume ratio of hydrogen/oil is within a range of 100-900, more preferably within a range of 300-700; and the volume space velocity is within a range of 0.5-3 h⁻¹, more preferably within a range of 0.8-2 h⁻¹. In the method provided by the present invention, the gas-phase hydrodesulfurization reaction is carried out according to the preferred volume ratio of hydrogen/oil, it is more conducive to reducing the partial pressure of the raw materials and realizing the complete vaporization of the raw materials. In addition, the gas-phase desulfurization reaction can be implemented under a lower pressure, so that the energy consumption is greatly saved.

[0028] It should be noted that during the gas-phase desulfurization reaction in step (1), both sulfur and nitrogen in the hydrocarbon oil raw material will be removed.

[0029] The type of the gas-phase hydrogenation reactor is not particularly limited in the present invention, preferably, the gas-phase hydrogenation reactor is a fixed-bed reactor.

[0030] In step (2) of the present invention, the gas-phase desulfurization reaction product is pressurized, and the pressurizing can be performed by using a pressurizing device such as a compressor, and the type of the compressor is not particularly limited, the examples include a reciprocating compressor, or a centrifugal compressor.

[0031] The present invention has a wider selection range of pressurizing the gas-phase desulfurization reaction product, and preferably pressurizing the gas-phase desulfurization reaction product to meet the requirements of ensuring normal feeding of the liquid-phase hydrogenation reactor and meeting the operating pressure of the liquid-phase hydrogenation reactor. The present invention promotes the synchronous liquefaction of hydrogen gas and petroleum products by pressurizing the gas-phase desulfurization reaction product, and because the dissolution rules of hydrogen and hydrogen sulfide in the petroleum products are different, namely the hydrogen solubility is high and the hydrogen sulfide solubility is low under the high-temperature condition, the hydrogen concentration in the liquefied liquid-phase is high and the hydrogen sulfide concentration is low when entering the subsequent liquid-phase hydrogenation reactor, the influence of hydrogen sulfide on the activity of a catalyst is avoided, and the arrangement of steam stripping and hydrogen sulfide removal device between two reactors is also saved.

[0032] According to a preferred embodiment of the present invention, the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2-10MPa, preferably 2.5-7.5 MPa. The choice of the pressurizing ranges may vary for different hydrocarbon raw materials and various product requirements.

[0033] Preferably, the hydrocarbon oil raw material is inferior diesel, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 4.5-6.5 MPa. In the preferred embodiment, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst. When the hydrocarbon oil raw material is inferior diesel, the method avoids the defects that deep desulfurization and dearomatization are arranged in the same reaction system and the reaction conditions are difficult to be compatible. By controlling the reaction conditions of the gas-phase hydrogenation reactor, aromatic ring-containing substances are not easy to adsorb on the surface of the catalyst, the competitive adsorption of aromatic hydrocarbon substances is greatly reduced, and the targeted desulfurization reaction is facilitated. At the same time, controlling the reaction conditions of the gas-phase hydrogenation reactor not only facilitates the gas-phase desulfurization, but also provides desirable synergy with the liquid-phase hydrogenation reactor, which is more conducive to the subsequent deep aromatization process.

[0034] According to another preferred embodiment of the invention, the hydrocarbon oil raw material is inferior diesel, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 4-7 MPa. In the preferred embodiment, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a deep hydrodesulfurization catalyst. In the preferred embodiment, the method of the present invention can be used for effectively removing macromolecular sulfides at relatively low temperature and appropriate pressure, if the removal of polycyclic aromatic hydrocarbons are additionally required, those skilled in the art can select a deep hydrodesulfurization catalyst (e.g., a Mo-Ni catalyst) with the additional function of removing polycyclic aromatic hydrocarbons to produce the high-quality diesel products.

[0035] According to another preferred embodiment of the present invention, the hydrocarbon oil raw material is aviation kerosene and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2.5-4 MPa. In the preferred embodiment, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst. When the hydrocarbon oil raw material is aviation kerosene, the method of the present invention can effectively remove aromatic hydrocarbons in the aviation kerosene, and improve the smoke point of the aviation kerosene, particularly when the content of aromatic hydrocarbons in the raw material is increased for the sake of increasing production of aviation kerosene and cutting the heavy component from the aviation kerosene distillate, the method can be more preferably suitable for the reaction environment of removing aromatic hydrocarbons, thereby implementing production of the aviation kerosene with a high smoke point.

[0036] According to another preferred embodiment of the present invention, the hydrocarbon oil raw material is aviation kerosene and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2.5-4 MPa. In

the preferred embodiment, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydroisomerization catalyst. When the hydrocarbon oil raw material is aviation kerosene, the method of the present invention can effectively isomerize branched chain alkane in the aviation kerosene, particularly when the content of long-chain alkane in the raw material is increased for the sake of increasing production of aviation kerosene and cutting the heavy component from the aviation kerosene distillate, the method can be more preferably suitable for the reaction environment of alkane isomerization, thereby implementing production of the aviation kerosene with a low freezing point.

[0037] According to another preferred embodiment of the present invention, the hydrocarbon oil raw material is wax oil, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 5-10 MPa. In the preferred embodiment, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is an isomerization hydrodewaxing catalyst. In this preferred embodiment, the method of the present invention can isomerize long-chain alkane in the wax oil fraction to improve the viscosity index of the specific petroleum product. When the hydrocarbon oil raw material is wax oil, the method preferably further comprises discharging a gas-phase component of the pressurized material flow upward out of a liquid-phase hydrogen reactor, optionally subjected to an impurity removal treatment to obtain a hydrogenated light component, and then mixing the hydrogenated light component and the liquid-phase hydrogenation reaction product to perform a hydrodearomatization reaction to obtain a specific petroleum product, such as white oil. The hydrogenation and dearomatization reaction may be carried out in a third hydrogenation reactor in the presence of a hydrogenation and dearomatization catalyst, and the form of the third hydrogenation reactor is not particularly limited in the present invention and may be a fixed-bed hydrogenation reactor. The reaction conditions are selected within a wide range as long as the hydrogenation and dearomatization can be smoothly carried out.

[0038] The second hydrogenation catalyst of the present invention may be selected from a wide range of types as long as the above purpose can be fulfilled, for example, the catalyst may be a hydrodearomatization catalyst having a hydrodearomatization function, a hydroisomerization catalyst having a hydroisomerization function, a deep hydrodesulfurization catalyst having a hydrogenation desulfurization function, and an isomerization hydrodewaxing catalyst having an isomerization hydrodewaxing function.

[0039] According to a preferred embodiment of the present invention, the hydrodearomatization catalyst may be a non-noble metal catalyst or a noble metal catalyst, and the non-noble metal catalyst may comprise a carrier and a hydrogenation active metal, wherein the carrier is an inorganic refractory oxide and is generally one or more selected from the group consisting of alumina, amorphous silica-alumina, silica, and titanium oxide, preferably alumina; the hydrogenation active metal comprises a VIB group metal component and/or a VIII group metal component. In the hydrodearomatization catalyst, the VIB group metal component is preferably selected from tungsten and/or molybdenum, the content of the VIB group metal component calculated in terms of oxide by mass in the catalyst is 5-30%, preferably 15-30%; the VIII group metal component is preferably selected from nickel and/or cobalt, and the content of the VIII group metal component calculated in terms of oxide by mass in the catalyst is 1-6%, preferably 2-5%. The hydrodearomatization catalyst may further comprise an auxiliary component, such as at least one selected from the group consisting of phosphorus, silicon, boron, magnesium, and fluorine, and the mass content of the auxiliary component in the catalyst having a hydrodesulfurization function is generally less than 6 wt%. The hydrodearomatization catalyst is preferably a Mo-Ni-type catalyst.

[0040] The hydrodearomatization catalyst may be voluntarily prepared with any method or maybe a commercially available catalyst, for example, at least one of the FHUDES-10, FHUDES-6, and FHUDES-8 catalysts researched and developed by the SINOPEC Fushun Research Institute of Petroleum and Petrochemical (FRIPP).

[0041] The noble metal catalyst preferably uses Pt, Pd, and the like as the active metal, and the noble metal catalyst can be voluntarily prepared with any method, or may be a commercially available catalyst, such as the FHDA-10 catalyst researched and developed by the SINOPEC Fushun Research Institute of Petroleum and Petrochemical (FRIPP).

[0042] According to a preferred embodiment of the present invention, the hydroisomerization catalyst may be any catalyst capable of performing a hydroisomerization function, and preferably, the catalyst is supported by the carrier alumina added with a molecular sieve (including but not limited to at least one of ZSM-5 molecular sieve, Y molecular sieve, and β molecular sieve), and uses a group VIII metal as an active component (including but not limited to Ni), the catalyst may be voluntarily prepared with any method or maybe a commercially available catalyst, for example, an FDW-3 catalyst researched and developed by the SINOPEC Fushun Research Institute of Petroleum and Petrochemical (FRIPP).

[0043] According to a preferred embodiment of the present invention, the deep hydrodesulfurization catalyst may be any catalyst capable of achieving the function of removing large molecular sulfur, the carrier of the catalyst is preferably alumina, and use the group VIB metal and the group VIII metal as the active component, the selections of said group VIB metal and group VIII metal are as described above, the catalyst may be voluntarily prepared with any method or maybe a commercially available catalyst, for example, one of FHUDES-5 and FHUDES-7 catalysts researched and developed by the SINOPEC Fushun Research Institute of Petroleum and Petrochemical (FRIPP).

[0044] The selection of the isomerization hydrodewaxing catalyst is not particularly limited in the present invention, the catalyst may be various isomerization hydrodewaxing catalysts conventionally used in the prior art. The specific selection range of its active components and carrier can be the same as those of the hydroisomerization catalysts, the details are not repeatedly described herein.

[0045] It should be noted that the catalyst having a certain function described in the present invention does not mean that the catalyst can only perform such a function, but mainly performs such a function, for instance, the hydrodesulfurization catalyst does not mean that it can only perform the hydrodesulfurization function, but mainly implements the hydrodesulfurization function in the application environment thereof.

[0046] According to a preferred embodiment of the present invention, the pressure of the liquid-phase hydrogenation reaction is higher than the pressure of the gas-phase hydrodesulfurization by at least 1MPa, preferably 1.5-7 MPa, and more preferably 2.5-6 MPa. The method provided by the present invention can be used for carrying out the reaction under medium and low pressure, thereby greatly reducing the reaction severity and saving energy consumption.

[0047] According to the method provided by the present invention, preferably, the conditions of the liquid-phase hydrogenation reaction comprise: the pressure is within a range of 2-8 MPa, more preferably within a range of 3-6 MPa; the temperature is within a range of 200-400°C, more preferably 260-360°C, and the volume space velocity is within a range of 0.1-3 h⁻¹, more preferably 0.5-1 h⁻¹.

[0048] The type of the liquid-phase hydrogenation reactor is not particularly limited in the present invention, preferably, the liquid-phase hydrogenation reactor is a fixed-bed reactor.

[0049] According to a preferred embodiment of the present invention, the liquid-phase hydrogenation reactor is a fixed-bed reactor provided with a gas-liquid separation area. The gas-liquid separation area may be any area capable of achieving separation and may be, for example, a flash evaporation area, that is, the liquid-phase hydrogenation reactor is a fixed-bed reactor provided with a flash evaporation area.

[0050] Specifically, a flash evaporation area is disposed in the liquid-phase hydrogenation reactor, a catalyst is not filled in the flash evaporation area or above, a liquid-phase hydrolysis reaction area is arranged below the flash evaporation area, a material flow (gas-liquid mixed phase) obtained after pressurizing a gas-phase desulfurization reaction product is fed into the flash evaporation area of the liquid-phase hydrogenation reactor, the obtained gas-phase component is upwards discharged from the liquid-phase hydrogenation reactor, the obtained liquid-phase components flow downwards and subject to a liquid-phase hydrogenation reaction, and the obtained liquid-phase hydrolysis reaction product (i.e., a hydrogenated heavy component) is discharged from the bottom of the liquid-phase hydrogenation reactor.

[0051] According to a preferred embodiment of the present invention, a gas-phase component of the pressurized material flow is discharged upwardly out of a liquid-phase hydrogenation reactor, optionally subjecting to an impurity removal treatment to obtain a hydrogenated light component.

[0052] The present invention has a wide selection range of impurity removal treatments, including but not limited to hydrogen sulfide removal treatments. Preferably, the impurity removal treatment comprises hydrogen sulfide removal treatment, more preferably comprises: subjecting the gas-phase component to a heat exchange and then a high-pressure separation to obtain the hydrogenated light component and a hydrogen containing hydrogen sulfide. According to the method provided by the present invention, among the gas-phase desulfurization reaction product, the reacted small molecules are not liquefied in the pressurizing process and are liquefied only through a heat exchanger and high-pressure separation, such a liquefying means is favorable for separating hydrogen gas from raw materials, can recover a large amount of hydrogen for recycling and improve the utilization rate of the hydrogen. The hydrogenated light component separated under high pressure can enter a subsequent stream stripping and fractionation system after mixing with the hydrogenated heavy component. The whole reaction system does not need a hydrogen compressor in a fixed-bed reaction system and a circulating oil pump in a liquid-phase hydrogenation reaction system, thereby decreasing the investment cost, simplifying the technological process, improving the reaction efficiency, and reducing the reaction severity.

[0053] The heat exchange may be carried out in a heat exchanger. The high-pressure separation may be performed in a high-pressure separator. The conditions for the heat exchange and the high-pressure separation are not particularly limited in the present invention as long as the above-mentioned purpose can be fulfilled.

[0054] Preferably, the heat exchange cools the gas-phase component to a temperature range of 100-200°C, more preferably a temperature range of 120-150°C.

[0055] According to a preferred embodiment of the present invention, the method further comprises: mixing the liquid-phase hydrogenation reaction product (also referred to as hydrogenated heavy component) and the hydrogenated light component to obtain a hydrogenation product.

[0056] According to a preferred embodiment of the present invention, the method further comprises subjecting the hydrogenation product to stream stripping (to remove hydrogen sulfide) and fractional distillation to obtain the target product. The specific conditions for the stream stripping and fractional distillation are not particularly limited and may be operated according to the raw materials and the performance requirements of the target product. For example, when the hydrocarbon oil raw material is poor-quality diesel, the hydrogenation product is subjected to stream stripping and

fractional distillation, and the naphtha fraction is cut to obtain a refined diesel product.

[0057] Preferably, the hydrogenation product is a refined diesel product, wherein the refined diesel product has a polycyclic aromatic hydrocarbon content of less than 5wt% and S content of less than 10 $\mu\text{g/g}$.

[0058] Preferably, the hydrogenation product is a refined aviation kerosene product, wherein the refined aviation kerosene product has a smoke point of more than 26mm, and/or a freezing point below -50°C .

[0059] Preferably, the hydrogenation product is a special petroleum product, wherein the special petroleum product has an aromatic hydrocarbon content of less than 5wt% and S content of less than 10 $\mu\text{g/g}$.

[0060] The second aspect of the present invention provides a hydrogenation system of hydrocarbon oil, the system comprises a gas-phase hydrogenation reactor, a pressurizing device and a liquid-phase hydrogenation reactor connected in sequence, wherein the gas-phase hydrogenation reactor is filled with a first hydrogenation catalyst, and the liquid-phase hydrogenation reactor is filled with a second hydrogenation catalyst;

the gas-phase hydrogenation reactor is used for carrying out a gas-phase desulfurization reaction of the hydrocarbon oil raw material and hydrogen gas to obtain a gas-phase desulfurization reaction product;

the pressurizing device is used for pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;

the liquid-phase hydrogenation reactor is used for contacting the pressurized material flow with the second hydrogenation catalyst to perform a liquid-phase hydrogenation reaction to obtain a liquid-phase hydrogenation reaction product.

[0061] Preferably, the pressurizing device is used for pressurizing the gas-phase desulfurization reaction product to a pressure range of 2-10 MPa, preferably 2.5-7.5 MPa. The type of the pressurizing device is not particularly limited in the present invention, for example, the pressurizing device may be a compressor, and the type of the compressor is not particularly limited, the examples include a reciprocating compressor or a centrifugal compressor.

[0062] In the system provided by the present invention, the types of the first hydrogenation catalyst and the second hydrogenation catalyst can be arranged according to the type of the hydrocarbon oil raw material, and the specific standard can be selected according to the content of the first aspect, the details are not repeatedly described herein.

[0063] Preferably, the hydrocarbon oil raw material is diesel oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst; or

[0064] The hydrocarbon oil raw material is diesel oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a deep hydrodesulfurization catalyst; or

[0065] The hydrocarbon oil raw material is aviation kerosene, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst; or

[0066] The hydrocarbon oil raw material is aviation kerosene, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydroisomerization catalyst; or

[0067] The hydrocarbon oil raw material is wax oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is an isomerization hydrodewaxing catalyst.

[0068] The specific selections of the first hydrogenation catalyst and the second hydrogenation catalyst may be the same as those in the first aspect, the details will not be repeatedly described herein.

[0069] According to the system provided by the present invention, preferably, the gas-phase hydrogenation reactor is a fixed-bed reactor.

[0070] According to a preferred embodiment of the present invention, a gas-phase component outlet is provided at the upper part of the liquid-phase hydrogen reactor, and a liquid-phase hydrogenation reaction product outlet is disposed at the bottom thereof.

[0071] According to the system provided by the present invention, the liquid-phase hydrogenation reactor is preferably a fixed-bed reactor, more preferably a fixed-bed reactor provided with a gas-liquid separation area. Specifically, the gas-liquid separation area may be any area capable of performing separation, such as a flash evaporation area, that is, the liquid-phase hydrogenation reactor is a fixed-bed reactor provided with a flash evaporation area. In particular, the liquid-phase hydrogenation reactor is provided with a flash evaporation area, the catalyst is not filled in the flash evaporation area and above, and a liquid-phase hydrogenation reaction area is arranged below the flash evaporation area, that is, the gas-liquid separation area is preferably positioned above the liquid-phase reaction area. The material flow (a gas-liquid mixed phase) obtained after pressurizing the gas-phase desulfurization reaction product is fed into a flash evaporation area of a liquid-phase hydrogenation reactor, the obtained gas-phase component is discharged upwards from an upper outlet of the liquid-phase hydrogenation reactor, the obtained liquid-phase component flows downwards to perform a liquid-phase hydrogen reaction, the obtained liquid-phase hydrogen reaction product (i.e., a hydrogenated heavy component) is discharged from a bottom outlet of the liquid-phase hydrogenation reactor.

[0072] According to a preferred embodiment of the present invention, the system further comprises an impurity removal device, wherein an inlet of the impurity removal device is in communication with a gas-phase component outlet of the

liquid-phase hydrogenation reactor for subjecting the gas-phase component in the pressurized material flow discharged from the liquid-phase hydrogenation reactor to treatment of removing impurities to obtain a hydrogenated light component.

[0073] Preferably, the impurity removal device is a hydrogen sulfide removal device.

[0074] Preferably, the hydrogen sulfide removal device comprises a heat exchanger and a high-pressure separation device which are communicated.

[0075] According to the system provided by the present invention, preferably, a gas-phase component outlet of the liquid-phase hydrogenation reactor is communicated with an inlet of the heat exchange, and an outlet of the heat exchange is communicated with an inlet of the high-pressure separation device. The gas-phase component is subjected to heat exchange and high-pressure separation to obtain the hydrogenated light component and the hydrogen containing hydrogen sulfide. The hydrogen-rich gas obtained after processing the hydrogen containing hydrogen sulfide is recyclable.

[0076] Preferably, the heat exchanger is used to cool down the gas-phase component, preferably cool the gas-phase component to a temperature range of 100-200°C, more preferably a temperature range of 120-150°C.

[0077] According to a preferred embodiment of the present invention, the system further comprises a mixing device for receiving and mixing the liquid-phase hydrogenation reaction product and the hydrogenated light component to obtain a hydrogenation product.

[0078] Specifically, a gas-phase component outlet of the liquid-phase hydrogenation reactor is sequentially connected with the heat exchanger and the high-pressure separator, and a liquid-phase outlet pipeline at the bottom of the liquid-phase hydrogenation reactor is connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator the gas-phase component, and the liquid-phase components are jointly fed into the mixing device.

[0079] According to a preferred embodiment of the present invention, the system further comprises a stream stripping and fractionation device for stripping (removing hydrogen sulfide) and fractionating the hydrogenation products. The specific conditions of the stream stripping and fractionation are not particularly limited and may be operated according to the raw materials and the performance requirements of the target product. Specific grounds may be as described above.

[0080] When the hydrocarbon oil raw material is wax oil, the system preferably further comprises a third hydrogenation reactor filled with a third hydrogenation catalyst (preferably is a hydrodearomatization catalyst), an inlet of the third hydrogenation reactor is in communication with a liquid-phase hydrogenation reaction product outlet of the third hydrogenation reactor, and a hydrogenated light component outlet of the impurity removal device, such that the hydrogenated light component and the liquid-phase hydrogenation reaction product carry out a hydrogenation dearomatization reaction.

[0081] The schemes and effects of the present invention are further described below with reference to the examples.

[0082] Unless otherwise specified in the present invention, the percentage and percentage content are denoted by mass.

[0083] The method and system of the present invention were described in detail below with reference to FIG. 1. The examples were given by using diesel oil as the hydrocarbon oil raw material. The diesel feedstock and hydrogen gas 1 entered a gas-phase hydrogenation reactor 2 (also called as a first hydrogenation reactor) to carry out a gas-phase desulfurization reaction to obtain a gas-phase desulfurization reaction product 3; the gas-phase desulfurization reaction product 3 entered into a pressurizing device 4 (compressor), it was pressurized by the compressor and the pressurized gas-phase desulfurization reaction product 3 flowed into a liquid-phase hydrogenation reactor 5 (also called a second hydrogenation reactor) provided with a flash evaporation area, wherein the liquid-phase components flowed downwards to enter into a reaction area to carry out a hydrogenation dearomatization reaction to obtain a liquid-phase hydrogenation reaction product 6 (hydrogenated heavy component); a gas-phase component 7 was discharged out of the liquid-phase hydrogenation reactor and introduced into a heat exchanger 8, then entered a high pressure separation device 9 for separation into a hydrogenated light component 11 and hydrogen containing hydrogen sulfide 10, the liquid-phase hydrogenation reaction product 6 and the hydrogenated light component 11 were mixed and the mixture was introduced into a stripping and fractionation device 12, and a refined diesel product 13 was finally obtained.

Examples 1-3

[0084] The method was carried out according to a schematic diagram of the technological process as shown in FIG. 1. Two fixed-bed hydrogenation reactors with a volume of 100mL were connected in series, namely a gas-phase hydrogenation reactor, and a liquid-phase hydrogenation reactor, respectively. A conventional power reciprocating compressor was arranged between the two reactors. The gas-phase hydrogenation reactor was filled with 50mL of a Mo-Co type diesel oil hydrogenation catalyst A, the liquid-phase hydrogenation reactor was filled with 50mL of a Mo-Ni type diesel oil hydrogenation catalyst B, and a flash evaporation area was disposed at the upper part of the liquid-phase hydrogenation reactor. A gas-phase component outlet was arranged at the top of the liquid-phase hydrogenation reactor and was sequentially connected with a heat exchanger (which cooled the gas-phase component to 130°C) and a high-pressure separator, a liquid-phase outlet was disposed at the bottom of the liquid-phase hydrogenation reactor, a liquid-phase outlet pipeline was connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator and jointly entered the subsequent stripping and fractionation device to cut out the naphtha fraction, a refined diesel product (with

an initial boiling point of 150°C) was obtained.

[0085] The mixed oil of straight-run diesel, coked diesel, and catalyzed diesel was used as the raw material. The catalyst properties were shown in Table 1, the feedstock oil properties were shown in Table 2, and the reaction process conditions and results were shown in Table 3.

Comparative Example 1

[0086] A hydrogenation reactor (i.e., a first hydrogenation reactor) was arranged according to the conventional diesel oil fixed-bed hydrogenation technological process. According to a traditional catalyst grading system, a mode of filling the Mo-Ni type catalyst B at the upper part and filling the Mo-Co type catalyst A at the lower part was adopted, and the filling volumes were 50 mL respectively. The high-fractionation, low-fractionation, steam stripping, and other technological processes behind the reactor were normally arranged to obtain a diesel product. The hydrogen after removing hydrogen sulfide was pressurized by the recycle hydrogen compressor for recycling. The raw materials and catalyst properties were the same as those in Examples 1-3, the reaction process conditions and results were shown in Table 3.

Comparative Example 2

[0087] A hydrogenation reactor (i.e., a first hydrogenation reactor) was arranged according to the conventional diesel oil fixed-bed hydrogenation technological process. According to the grading sequences of catalysts as same as those in Examples 1-3, a mode of filling the Mo-Co type catalyst A at the upper part and filling the Mo-Ni type catalyst B at the lower part was adopted, and the filling volumes were 50 mL respectively. The high-fractionation, low-fractionation, steam stripping, and other technological processes behind the reactor were normally arranged to obtain a diesel product. The hydrogen after removing hydrogen sulfide was pressurized by the recycle hydrogen compressor for recycling. The raw materials and catalyst properties were the same as those in Examples 1-3, the reaction process conditions and results were shown in Table 3.

Comparative Example 3

[0088] Two hydrogenation reactors (i.e., a first hydrogenation reactor and a second hydrogenation reactor) were connected in series according to the conventional diesel oil fixed-bed hydrogenation technological process, and a stripping tower was arranged between the two reactors. 50 mL of the Mo-Co type catalyst A was filled in the first hydrogenation reactor 1, and 50 mL of the Mo-Ni type catalyst B was filled in the second hydrogenation reactor 2. The high-fractionation, low-fractionation, steam stripping, and other technological processes behind the reactors were normally arranged to obtain a diesel product. The hydrogen after removing hydrogen sulfide was pressurized by the recycle hydrogen compressor for recycling. The raw materials and catalyst properties were the same as those in Examples 1-3, the reaction process conditions and results were shown in Table 3.

Comparative Example 4

[0089] The same hydrogenation technology process as those of Examples 1-3 was used, except that a high-power reciprocating compressor was installed between the first hydrogenation reactor and the second hydrogenation reactor, and the process conditions were controlled, the reaction process conditions and results were shown in Table 3.

Table 1 Physicochemical properties of the catalysts

Catalyst No.	A	B
Product brand	FHUDS-7	FHUDS-8
Active metal	Mo-Co	Mo-Ni
MoO ₃ , wt%	20	24
NiO or CoO, wt%	3.5	5.0
Shape	Clover	Clover
Diameter, mm	1.2	1.2
Specific surface area, m ² ·g ⁻¹	180	180
Pore volume, mL·g ⁻¹	0.35	0.35

Table 2 Properties of the feedstock oil

Properties of petroleum product	
Density (20°C), g·cm ⁻³	0.89
Distillation range, °C	180-370
S, μg·g ⁻¹	10360
N, μg·g ⁻¹	713
Aromatic hydrocarbons, wt%	63.5
Polycyclic aromatic hydrocarbons, wt%	32.2
Monocyclic aromatic hydrocarbon, wt%	31.3

Table 3 Hydrogenation process conditions and results

	Examp le 1	Examp le 2	Examp le 3	Comparativ e Example 1	Comparativ e Example 2	Comparativ e Example 3	Comparativ e Example 4
First hydrogenation reactor							
Pressure, MPa	0.5	0.5	1.0	6.5	6.5	6.5	3.5
Temperature, °C	370	375	380	370	360	380	350
The volume ratio of hydrogen/oil, v/v	500	500	500	500	500	500	1080
Volume space velocity, h ⁻¹	1.0	1.0	1.0	0.5	0.5	1.0	1.0
Second hydrogenation reactor							
Pressure, MPa	4	5	6	-	-	6.5	10.0
Temperature, °C	300	320	340	-	-	360	320
Volume space velocity, h ⁻¹	0.5	0.6	0.7	-	-	1.0	0.5
Properties of refined diesel product							
S, μg/g	9.0	7.3	6.1	5.3	18.1	8.1	73.3
N, μg/g	5.3	4.2	3.9	3.2	7.3	5.0	17.7
Polycyclic aromatic hydrocarbons , wt%	4.9	4.1	3.7	11.7	8.7	7.1	19.6

[0090] As illustrated by Table 3, the conventional fixed-bed hydrogenation technology and the traditional catalyst filling system were adopted in Comparative Example 1, the hydrogenation of polycyclic aromatic hydrocarbons was carried out at the upper part of the reactor, the deep desulfurization was performed at the lower part of the reactor, and in order to achieve the deep desulfurization effect, the hydrogenation reaction conditions of aromatic hydrocarbons can hardly be taken into consideration, and the effect of removing the polycyclic aromatic hydrocarbons is poor. In contrast, the pressure of the reaction system in the present invention is significantly reduced, and because the desulfurization and dearomatization were divided into two reaction systems, the reaction conditions can be optimized in a targeted manner to produce a better dearomatization effect.

[0091] The fixed-bed hydrogenation technology of Comparative Example 2 adopted the same catalyst loading sequence as in the Examples, the sulfides were removed at the upper part of the reactor, and the aromatic hydrocarbon

hydrogenation saturation reaction was implemented in the lower part of the reactor, both the sulfide removal effect and the aromatic hydrocarbon hydrogenation effect were poor due to large temperature rise at the bottom of the reactor, and the thermodynamic limitation imposed on the hydrogenation of aromatic hydrocarbons.

[0092] The two reactors used in Comparative Example 3 were conventional fixed-bed hydrogenation reactors, the reaction conditions were severe, and both the hydrogen consumption and energy consumption were high; in addition, given that the effluent of the first reactor completely entered the second reactor, so that the space velocity of the aromatic hydrocarbon hydrogenation in the second reactor was increased, the effect of removing the polycyclic aromatic hydrocarbons was deteriorated.

[0093] In Comparative Example 4, since the hydrogen-oil ratio of the gas-phase hydrogenation reactor was too high, the partial pressure of the feedstock oil was reduced, and the adsorption of sulfides on the surface of the catalyst was affected, thus the desulfurization effect was not ideal. Meanwhile, the liquefaction difficulty of the gasified gas-phase reactor effluent was obviously increased, the heavy components can hardly be completely liquefied even at the high reaction pressure of 10MPa, thus the removal effect of the polycyclic aromatic hydrocarbon was influenced.

Example 4

[0094] The method was carried out according to a schematic diagram of the technological process as shown in FIG. 1. Two fixed-bed hydrogenation reactors with a volume of 100mL were connected in series, namely a gas-phase hydrogenation reactor, and a liquid-phase hydrogenation reactor, respectively. A conventional power reciprocating compressor was arranged between the two reactors. The gas-phase hydrogenation reactor was filled with 50mL of a Mo-Ni type hydrogenation catalyst A, the liquid-phase hydrogenation reactor was filled with 50mL of an isomerization catalyst B (with a product brand FDW-3), and a flash evaporation area was disposed at the upper part of the liquid-phase hydrogenation reactor. A gas-phase component outlet was arranged at the top of the liquid-phase hydrogenation reactor and was sequentially connected with a heat exchanger (which cooled the gas-phase component to 130°C) and a high-pressure separator, a liquid-phase outlet was disposed at the bottom of the liquid-phase hydrogenation reactor, a liquid-phase outlet pipeline was connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator and jointly entered the subsequent stripping and fractionation device.

[0095] The catalyst properties were shown in Table 4, the feedstock oil properties were shown in aviation kerosene 1 of Table 5, and the reaction process conditions and results were illustrated in Table 6.

Example 5

[0096] The method was carried out according to a schematic diagram of the technological process as shown in FIG. 1. Two fixed-bed hydrogenation reactors with a volume of 100mL were connected in series. A reciprocating compressor was arranged between the two reactors. The first reactor was a gas-phase hydrogenation reactor filled with 50mL of a Mo-Ni type diesel oil hydrogenation catalyst A, and the second reactor was the liquid-phase hydrogenation reactor filled with 50mL of Ni-based hydrogenation catalyst C, and a flash evaporation area was disposed at the upper part of the liquid-phase hydrogenation reactor. A gas-phase component outlet was arranged at the top of the second reactor and was sequentially connected with a heat exchanger (which cooled the gas-phase component to 130°C) and a high-pressure separator, a liquid-phase outlet pipeline at the bottom of the second reactor was connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator and jointly entered the subsequent stripping and fractionation device.

[0097] The catalyst properties were shown in Table 4, the feedstock oil properties were shown in aviation kerosene 2 of Table 5, and the reaction process conditions and results were illustrated in Table 6.

Example 6

[0098] The method was carried out according to a schematic diagram of the technological process as shown in FIG. 1. Two fixed-bed hydrogenation reactors with a volume of 100mL were connected in series, namely a first reactor and a second reactor, respectively. A conventional power reciprocating compressor was arranged between the two reactors. The first reactor was a gas-phase desulfurization reactor filled with 50mL of a Mo-Ni type diesel oil hydrodesulfurization catalyst D, the second reactor was a liquid-phase desulfurization reactor filled with 50mL of a Mo-Co type diesel oil hydrodesulfurization catalyst E, and a flash evaporation area was disposed at the upper part of the second reactor. A gas-phase component outlet was arranged at the top of the second reactor and was sequentially connected with a heat exchanger (which cooled the gas-phase component to 130°C) and a high-pressure separator, a liquid-phase outlet pipeline at the bottom of the second reactor was connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator, and jointly entered the subsequent stripping and fractionation device to cut out the naphtha fraction, a low sulfur diesel product (with an initial boiling point of 180°C) was obtained.

[0099] The catalyst properties were shown in Table 4, the feedstock oil properties were shown in diesel oil in Table 5, and the reaction process conditions and results were illustrated in Table 6.

Example 7

[0100] The method was carried out according to a schematic diagram of the technological process as shown in FIG. 2. Three fixed-bed hydrogenation reactors with a volume of 100mL were connected in series, namely a first reactor, a second reactor, and a third reactor, respectively. A conventional power reciprocating compressor was arranged between the first reactor and the second reactor. The first reactor was a gas-phase desulfurization reactor filled with 50mL of a Mo-Co type diesel oil hydrogenation catalyst E, the second reactor was a liquid-phase desulfurization reactor filled with 50mL of a Ni type isomerization hydrodewaxing catalyst B, and a flash evaporation area was disposed at the upper part of the second reactor. A gas-phase component outlet was arranged at the top of the second reactor and was sequentially connected with a heat exchanger (which cooled the gas-phase component to 130°C) and a high-pressure separator, a liquid-phase outlet pipeline at the bottom of the second reactor was connected with a liquid-phase outlet pipeline at the bottom of the high-pressure separator, and jointly entered the subsequent third reactor filled with 50mL of a Mo-Ni deep hydrogenation catalyst D, a special petroleum product was finally obtained.

[0101] The catalyst properties were shown in Table 4, the feedstock oil properties were shown in the wax oil in Table 5, and the reaction process conditions and results were illustrated in Table 6.

Table 4 Physicochemical properties of the catalysts

Catalyst No.	A	B	C	D	E
Carrier	Al ₂ O ₃	ZSM-5-Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃
Active metal	Ni-Mo	Ni	Ni	Mo-Ni	Mo-Co
NiO or CoO, wt%	4.5	2.2	20	24	20
MoO ₃ or WO ₃ , wt%	15	-	-	5	3.5
Shape	Clover	Cylindrical strip	Clover	Clover	Clover
Diameter, mm	2.0	1.4~1.6	1.2	1.2	1.2
Specific surface area, m ² ·g ⁻¹	170	180	100	180	180
Pore volume, mL·g ⁻¹	0.45	0.40	0.55	0.35	0.35

Table 5 Properties of the feedstock oil

Properties of petroleum product	Aviation kerosene 1	Aviation kerosene 2	Diesel oil	Wax oil
Density (20°C), g·cm ⁻³	0.72	0.74	0.87	0.875
Distillation range, °C	140~300	150~300	180~370	180~513
S, μg·g ⁻¹	1735	1637	12130	3900
N, μg·g ⁻¹	20	10	769	-
Aromatic hydrocarbons, wt%				35
Smoke point, mm	22	20	-	-
Freezing point, °C	-45	-46	-	-

Table 6 Hydrogenation process conditions and results

	Example 4	Example 5	Example 6	Example 7
First hydrogenation reactor				
Pressure, MPa	0.5	1.0	1.0	2.0

(continued)

	Example 4	Example 5	Example 6	Example 7
First hydrogenation reactor				
Temperature, °C	260	250	370	370
The volume ratio of hydrogen/oil, v/v	300	300	500	500
Volume space velocity, h ⁻¹	1.0	3.0	1.0	1.0
Second hydrogenation reactor				
Pressure, MPa	5.0	4.0	6	9
Temperature, °C	320	140	370	360
Volume space velocity, h ⁻¹	0.2	1.0	0.7	0.75
Third hydrogenation reactor				
Pressure, MPa				7
Temperature, °C				340
Volume space velocity, h ⁻¹				1.5
Product				
S, µg/g	14.1	26	3.1	0.2
N, µg/g	1.3	2.6	0.9	-
Aromatic hydrocarbons, wt%				3.7
Freezing point, °C	-54.9	-49		
Smoke point, mm	24	27.6		

[0102] The above content describes in detail the preferred embodiments of the invention, but the invention is not limited thereto. A variety of simple modifications can be made in regard to the technical solutions of the invention within the scope of the technical concept of the invention, including a combination of individual technical features in any other suitable manner, such simple modifications and combinations thereof shall also be regarded as the content disclosed by the invention, each of them falls into the protection scope of the invention.

Claims

1. A hydrogenation method of hydrogen oil, is **characterized in that** the method comprises the following steps:

- (1) subjecting a hydrocarbon oil raw material to a gas-phase desulfurization reaction in a gas-phase hydrogenation reactor in the presence of hydrogen gas to obtain a gas-phase desulfurization reaction product;
- (2) pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;
- (3) feeding the pressurized material flow into a liquid-phase hydrogenation reactor, and subjecting liquid-phase components in the pressurized material flow to liquid-phase hydrogenation reaction in a liquid-phase hydrogenation reactor to obtain a liquid-phase hydrogenation reaction product.

2. The method according to claim 1, wherein the hydrocarbon oil raw material is at least one selected from the group consisting of inferior diesel, aviation kerosene, wax oil, and naphtha;

preferably, the inferior diesel has an initial boiling point of 150-200°C, an end boiling point of 320-400°C, S content not higher than 20,000 µg/g, more preferably not higher than 15,000 µg/g, N content not higher than 1,000 µg/g, more preferably not higher than 800 µg/g, and polycyclic aromatic hydrocarbon content not higher than 50 wt%;

preferably, the aviation kerosene has an initial boiling point of 80-150°C, an end boiling point of 200-300°C, S content not higher than 8,000 µg/g, more preferably not higher than 4,000 µg/g, N content not higher than 100

$\mu\text{g/g}$, more preferably not higher than $20 \mu\text{g/g}$;
 preferably, the wax oil has an initial boiling point of $160\text{--}220^\circ\text{C}$, an end boiling point of $300\text{--}400^\circ\text{C}$, S content not higher than $30,000 \mu\text{g/g}$, more preferably not higher than $20,000 \mu\text{g/g}$, N content not higher than $2,000 \mu\text{g/g}$, more preferably not higher than $1,500 \mu\text{g/g}$, and polycyclic aromatic hydrocarbon content not higher than 60 wt%.

3. The method according to claim 1 or 2, wherein the gas-phase desulfurization reaction is performed in the presence of a first hydrogenation catalyst, the first hydrogenation catalyst is a catalyst having a hydrodesulfurization function;

preferably, the conditions of the gas-phase desulfurization reaction comprise: the pressure is within a range of 0.1-2.8 MPa, more preferably within a range of 0.5-2 MPa; the temperature is within a range of $260\text{--}400^\circ\text{C}$, more preferably within a range of $320\text{--}390^\circ\text{C}$; the volume ratio of hydrogen/oil is within a range of 100-900, more preferably within a range of 300-700; and the volume space velocity is within a range of $0.5\text{--}3 \text{ h}^{-1}$, more preferably within a range of $0.8\text{--}2 \text{ h}^{-1}$;

preferably, the gas-phase hydrogenation reactor is a fixed-bed reactor.

4. The method according to any one of claims 1-3, wherein the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2-10MPa, preferably 2.5-7.5 MPa.

5. The method according to any one of claims 1-4, wherein the hydrocarbon oil raw material is inferior diesel, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 4.5-6.5 MPa; preferably, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst.

6. The method according to any one of claims 1-4, wherein the hydrocarbon oil raw material is inferior diesel, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 4-7 MPa; preferably, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a deep hydrodesulfurization catalyst.

7. The method according to any one of claims 1-4, wherein the hydrocarbon oil raw material is aviation kerosene, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2.5-4 MPa; preferably, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst.

8. The method according to any one of claims 1-4, wherein the hydrocarbon oil raw material is aviation kerosene, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 2.5-4 MPa; preferably, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is a hydroisomerization catalyst.

9. The method according to any one of claims 1-4, wherein the hydrocarbon oil raw material is wax oil, and the gas-phase desulfurization reaction product in step (2) is pressurized to a pressure of 5-10 MPa;

preferably, the liquid-phase hydrogenation reaction is performed in the presence of a second hydrogenation catalyst, and the second hydrogenation catalyst is an isomerization hydrodewaxing catalyst;

preferably, the method further comprises: discharging a gas-phase component of the pressurized material flow upward out of a liquid-phase hydrogen reactor, optionally subjecting to an impurity removal treatment to obtain a hydrogenated light component, then mixing the hydrogenated light component and the liquid-phase hydrogenation reaction product to perform a hydrodearomatization reaction.

10. The method according to any one of claims 1-9, the pressure of the liquid-phase hydrogenation reaction is higher than the pressure of the gas-phase hydrodesulfurization by at least 1MPa, preferably 1.5-7 MPa, and more preferably 2.5-6 MPa.

11. The method according to any one of claims 1-10,

wherein the liquid-phase hydrogenation reactor is a fixed-bed reactor, preferably a fixed-bed reactor provided with a gas-liquid separation area;

preferably, the conditions of the liquid-phase hydrogenation reaction comprise: the pressure is within a range

of 2-8 MPa, more preferably within a range of 3-6 MPa; the temperature is within a range of 200-400°C, more preferably 260-360°C, and the volume space velocity is within a range of 0.1-3 h⁻¹, more preferably 0.5-1 h⁻¹.

- 5 12. The method according to any one of claims 1-11, wherein a gas-phase component of the pressurized material flow is discharged upwardly out of a liquid-phase hydrogenation reactor, optionally subjecting to an impurity removal treatment to obtain a hydrogenated light component;

preferably, the impurity removal treatment comprises hydrogen sulfide removal treatment, more preferably comprises: subjecting the gas-phase component to a heat exchange and then a high-pressure separation to obtain the hydrogenated light component and a hydrogen containing hydrogen sulfide;
10 preferably, the heat exchange cools the gas-phase component to a temperature range of 100-200°C, more preferably a temperature range of 120-150°C.

- 15 13. The method according to claim 12, wherein the method further comprises: mixing the liquid-phase hydrogenation reaction product and the hydrogenated light component to obtain a hydrogenation product;

preferably, the hydrogenation product is a refined diesel product, wherein the refined diesel product has a polycyclic aromatic hydrocarbon content of less than 5wt% and S content of less than 10 µg/g;
20 preferably, the hydrogenation product is a refined aviation kerosene product, wherein the refined aviation kerosene product has a smoke point of more than 26mm, and/or a freezing point below -50°C;
preferably, the hydrogenation product is a special petroleum product, wherein the special petroleum product has an aromatic hydrocarbon content of less than 5wt%, and S content of less than 10 µg/g.

- 25 14. A hydrogenation system of hydrocarbon oil, the system comprises a gas-phase hydrogenation reactor, a pressurizing device, and a liquid-phase hydrogenation reactor connected in sequence, wherein the gas-phase hydrogenation reactor is filled with a first hydrogenation catalyst, and the liquid-phase hydrogenation reactor is filled with a second hydrogenation catalyst;

the gas-phase hydrogenation reactor is used for carrying out a gas-phase desulfurization reaction of the hydrocarbon oil raw material and hydrogen gas to obtain a gas-phase desulfurization reaction product;
30 the pressurizing device is used for pressurizing the gas-phase desulfurization reaction product to obtain a pressurized material flow;
the liquid-phase hydrogenation reactor is used for contacting the pressurized material flow with the second hydrogenation catalyst to perform a liquid-phase hydrogenation reaction to obtain a liquid-phase hydrogenation reaction product.
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15. The hydrogenation system according to claim 14, wherein the pressurizing device is used for pressurizing the gas-phase desulfurization reaction product to a pressure range of 2-10 MPa.

- 40 16. The hydrogenation system according to claim 14 or 15, wherein

the hydrocarbon oil raw material is diesel oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst; or
the hydrocarbon oil raw material is diesel oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a deep hydrodesulfurization catalyst; or
45 the hydrocarbon oil raw material is aviation kerosene, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydrodearomatization catalyst; or
the hydrocarbon oil raw material is aviation kerosene, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is a hydroisomerization catalyst; or
50 the hydrocarbon oil raw material is wax oil, the first hydrogenation catalyst is a hydrodesulfurization catalyst, and the second hydrogenation catalyst is an isomerization hydrodewaxing catalyst.

17. The hydrogenation system according to any one of claims 14-16,

55 the gas-phase hydrogenation reactor is a fixed-bed reactor;
the liquid-phase hydrogenation reactor is a fixed-bed reactor, preferably a fixed-bed reactor provided with a gas-liquid separation area.

18. The hydrogenation system according to any one of claims 14-17, the system further comprises an impurity removal device, wherein an inlet of the impurity removal device is in communication with a gas-phase component outlet of the liquid-phase hydrogenation reactor for subjecting the gas-phase component in the pressurized material flow discharged from the liquid-phase hydrogenation reactor to a treatment of removing impurities to obtain a hydrogenated light component;

preferably, the impurity removal device is a hydrogen sulfide removal device;
preferably, the hydrogen sulfide removal device comprises a heat exchanger and a high-pressure separation device which are communicated.

19. The hydrogenation system according to claim 18, wherein the system further comprises a mixing device for receiving and mixing the liquid-phase hydrogenation reaction product and the hydrogenated light component to obtain a hydrogenation product.

20. The hydrogenation system according to claim 18, wherein the hydrocarbon oil raw material is wax oil, the system further comprises a third hydrogenation reactor filled with a third hydrogenation catalyst, an inlet of the third hydrogenation reactor is in communication with a liquid-phase hydrogenation reaction product outlet of the third hydrogenation reactor and a hydrogenated light component outlet of the impurity removal device, such that the hydrogenated light component and the liquid-phase hydrogenation reaction product carry out a hydrogenation dearomatization reaction.

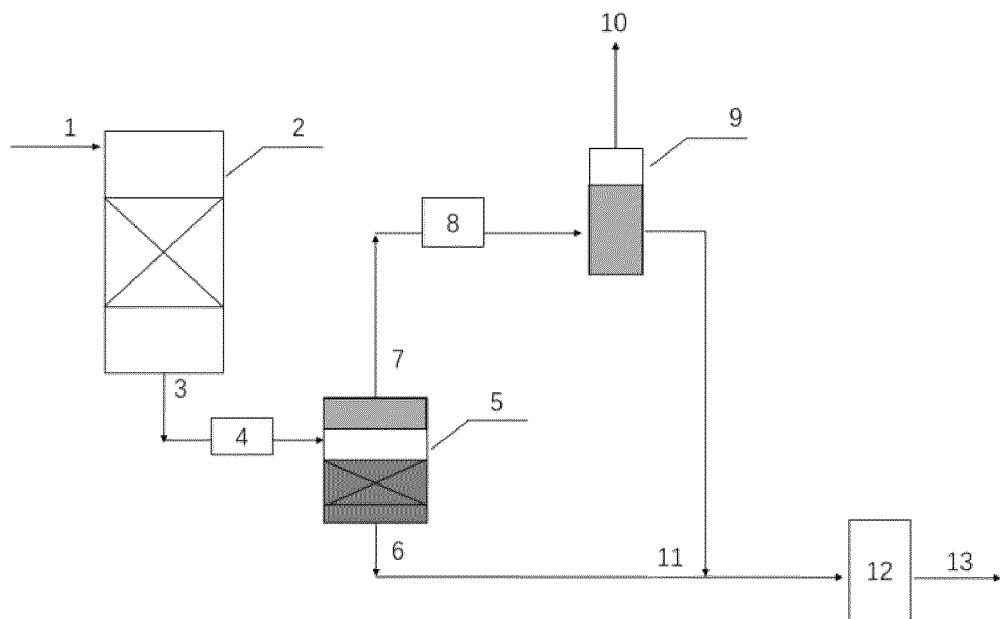


FIG. 1

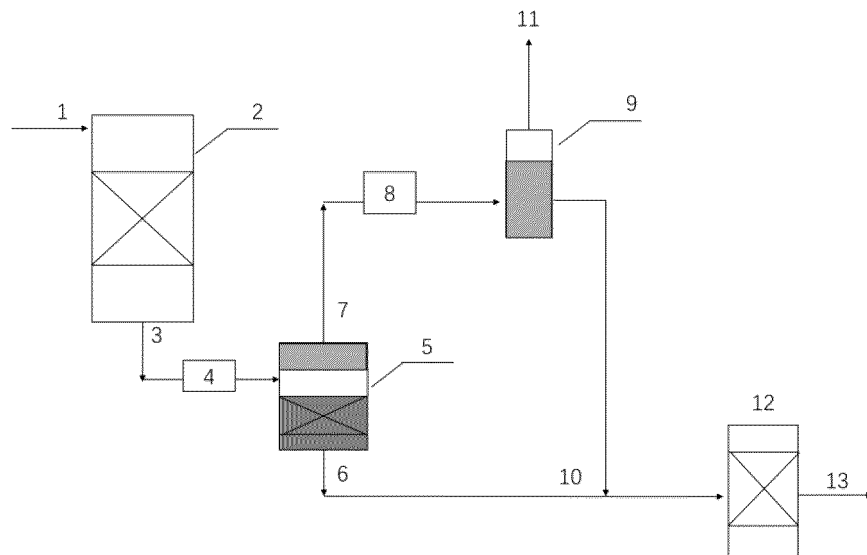


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/142685

A. CLASSIFICATION OF SUBJECT MATTER C10G65/02(2006.01)i; C10G45/02(2006.01)i; C10G45/44(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) C10G 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) DWPI, CNTXT, CNKI, 超星读秀, DUXIU: 烃油, 柴油, 加氢, 脱硫, 连续液相加氢, 脱芳烃, 芳烃饱和, 加压, 增压, hydrocarbon+, diesel, hydrogenation, hydrotreating, hydrodesulfurization, liquid-phase, continuous, aromatic saturation, pressure															
C. DOCUMENTS CONSIDERED TO BE RELEVANT															
<table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2009095656 A1 (KOKAYEFF PETER et al.) 16 April 2009 (2009-04-16) claim 14, description, paragraphs 12-22, and figure 1</td> <td>1-20</td> </tr> <tr> <td>A</td> <td>CN 101942327 A (CHINA PETROLEUM AND CHEMICAL CORP. FUSHUN RESEARCH INSTITUTE OF PETROLEUM AND PETROCHEMICALS) 12 January 2011 (2011-01-12) description, paragraphs 5-48</td> <td>1-20</td> </tr> <tr> <td>A</td> <td>CN 105038843 A (CHINA UNIVERSITY OF PETROLEUM (EAST CHINA)) 11 November 2015 (2015-11-11) description, paragraphs 6-50</td> <td>1-20</td> </tr> <tr> <td>A</td> <td>孙磊 (SUN, Lei). "炼油企业柴油质量升级方案及实施效果 (Non-official translation: Diesel Quality Upgrade Plan and Implementation Effect in Refinery Enterprises)" 石油炼制与化工 (Petroleum Processing and Petrochemicals), Vol. 49, No. 10, 31 October 2018 (2018-10-31), pages 25-31</td> <td>1-20</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2009095656 A1 (KOKAYEFF PETER et al.) 16 April 2009 (2009-04-16) claim 14, description, paragraphs 12-22, and figure 1	1-20	A	CN 101942327 A (CHINA PETROLEUM AND CHEMICAL CORP. FUSHUN RESEARCH INSTITUTE OF PETROLEUM AND PETROCHEMICALS) 12 January 2011 (2011-01-12) description, paragraphs 5-48	1-20	A	CN 105038843 A (CHINA UNIVERSITY OF PETROLEUM (EAST CHINA)) 11 November 2015 (2015-11-11) description, paragraphs 6-50	1-20	A	孙磊 (SUN, Lei). "炼油企业柴油质量升级方案及实施效果 (Non-official translation: Diesel Quality Upgrade Plan and Implementation Effect in Refinery Enterprises)" 石油炼制与化工 (Petroleum Processing and Petrochemicals), Vol. 49, No. 10, 31 October 2018 (2018-10-31), pages 25-31	1-20
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.															
<table border="0"> <tr> <td style="vertical-align: top;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family													
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Date of the actual completion of the international search 29 May 2023	Date of mailing of the international search report 04 June 2023														
Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/CN) China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088	Authorized officer Telephone No.														

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2022/142685

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Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US	2009095656	A1	16 April 2009	US 7790020 B2	07 September 2010
CN	101942327	A	12 January 2011	None	
CN	105038843	A	11 November 2015	None	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 202210008433 [0001]
- CN 108085058 B [0005]
- CN 109926067 A [0006]