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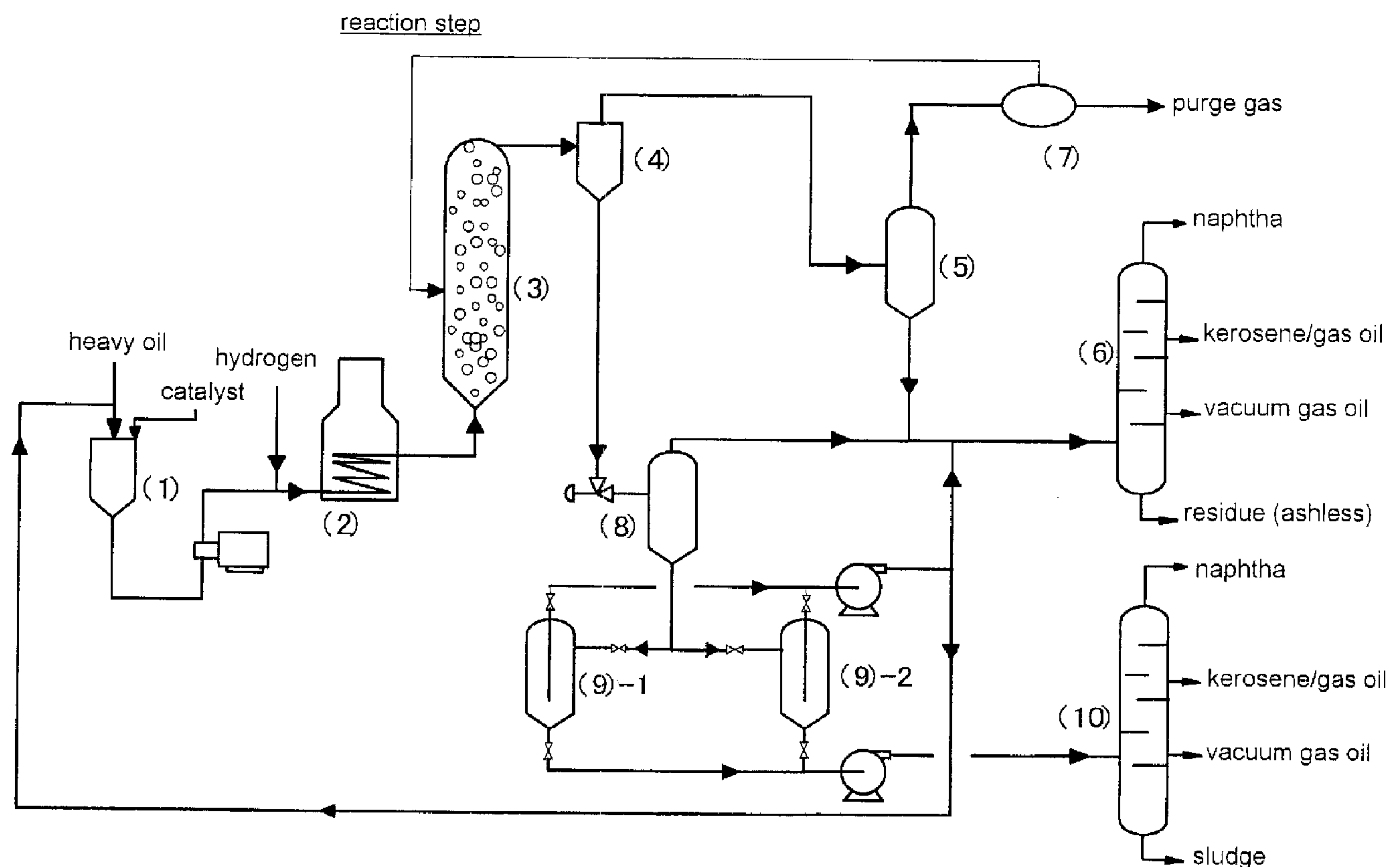
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(54) Titre : PROCÉDE D'HYDROCRAQUAGE DU PÉTROLE LOURD

(54) Title: PROCESS OF HYDROCRACKING PETROLEUM HEAVY OIL



(57) Abrégé/Abstract:

There is provided a hydrocracking process of a petroleum heavy oil containing a heavy metal, wherein hydrocracking is carried out in a suspended bed reactor with an iron based catalyst, which process allows selective TI removal without addition of a light solvent. in such process, (1) a reaction product from the reactor is divided, in a high pressure gas-liquid separator, into a gas phase

(57) **Abrégé(suite)/Abstract(continued):**

stream and a liquid phase stream under a pressure which is the same as that of the reactor at a temperature of 200°C to 350°C; (2) the obtained liquid phase stream is divided, in a low pressure gas-liquid separator, into a gas phase stream and a liquid phase stream under a pressure of normal pressure to 1 MPaG at a temperature of 190°C to 340°C; (3) the obtained liquid phase stream is supplied to a solid-liquid separator of a gravity settling type so as to settle under a pressure of normal pressure to 1 MPaG at a temperature of 190°C to 340°C, whereby an upper layer in the separator is withdrawn from the separator while a lower layer containing the solid component and an oil component is withdrawn from the separator; and (4) a portion or a whole of the obtained upper layer is recycled to the suspended bed reactor.

ABSTRACT OF THE DISCLOSURE

There is provided a hydrocracking process of a petroleum heavy oil containing a heavy metal, wherein hydrocracking is carried out in a suspended bed reactor with an iron based catalyst, which process allows selective
5 TI removal without addition of a light solvent.

In such process,

(1) a reaction product from the reactor is divided, in a high pressure gas-liquid separator, into a gas phase stream and a liquid phase stream under a pressure which is the
10 same as that of the reactor at a temperature of 200°C to 350°C;

(2) the obtained liquid phase stream is divided, in a low pressure gas-liquid separator, into a gas phase stream and a liquid phase stream under a pressure of normal
15 pressure to 1 MPaG at a temperature of 190°C to 340°C;

(3) the obtained liquid phase stream is supplied to a solid-liquid separator of a gravity settling type so as to settle under a pressure of normal pressure to 1 MPaG at a
20 temperature of 190°C to 340°C, whereby an upper layer in the separator is withdrawn from the separator while a lower layer containing the solid component and an oil component is withdrawn from the separator; and

(4) a portion or a whole of the obtained upper layer is
25 recycled to the suspended bed reactor.

SPECIFICATION

TITLE OF THE INVENTION

Process of Hydrocracking Petroleum Heavy Oil

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for hydrocracking a petroleum heavy oil, and particularly a petroleum heavy oil which contains a heavy metal component(s). Especially, the present invention relates to a process for hydrogenating, in the presence of a catalyst, a petroleum heavy oil which contains a heavy metal component(s) such as atmospheric residue, vacuum residue or the like, whereby a light product is produced.

15 Related Art

Heavy oil cracking techniques which produce a light

product, which tends to run short, from a redundant heavy oil have gotten a lot of attention in view of a rapid change of the oil demand situation wherein a lighter oil is increasingly required with a heavier crude oil being increasingly produced. The importance of such techniques has become increased more and more in the situation wherein the deposit of crude oil inevitably decreases.

A number of processes of thermal cracking or hydrocracking of the heavy oil have been proposed, but such processes include some problems as to cracking of the heavy oil such as vacuum residue and the like.

The above mentioned heavy oil tends to contain a rather large amount of nitrogen compounds and sulfur compounds, and further contain a large amount of organic metal impurities which are readily harmful to hydrocracking of the heavy oil in the presence of a catalyst. Many of such organic metal impurities (i.e. metal impurities) include nickel (Ni), vanadium (V) or the like, but the other metal(s) may often be contained therein. Those metal impurities chemically bond to organic compounds in a crude oil such as an asphaltene and the like of which molecular weight is rather large. Due to the presence of such impurities, a performance of the catalyst to crack and remove nitrogen containing compounds, sulfur containing compounds and oxygen containing compounds is considerably degraded.

As a technique to treat the heavy oil such as vacuum residue or the like without using a catalyst, so-called coking process which is a thermal cracking process is known. In addition to a processing problem of a large amount of formed coke as a by-product, the above coking process has a disadvantage in that an amount of produced gases is increased due to over-cracking so that a yield of produced distillate is inevitably reduced, and the distillate contains large amounts of aromatics and olefins, whereby a product quality of the distillate is bad.

In a hydrocracking process using a fixed bed reactor wherein catalyst particulates are filled, highly cracking is affected by asphaltenes and heavy metals such as Ni, V and so on which are contained in the feed material, so that coke as a by-product and heavy metals gradually deposit in the catalyst bed, whereby activity of the catalyst particulates is degraded and also the catalyst bed is clogged, which limits the continuous operation of the process for a long period.

In a hydrocracking process in an ebullated bed reactor in which granular catalysts formed by extrusion such as Co-Mo catalyst are used, there are more advantages than the fix bed reactor in that vigorous mixing in the ebullated bed reactor causes no problem about a pressure loss increase by means of deposition of the coke and the like, and also

that a long period continuous operation is possible with keeping the activity of the catalyst at a certain level during which withdrawal of the catalyst from the reactor and supply of new catalyst are possible. However, the ebullated bed reactor has mechanical problems as to, for example, a pump and the like because of recycling the catalyst, which makes the process operation more difficult than in the case of the fixed bed reactor. Further, with such ebullated bed reactor, the catalyst is expensive, a pressure for the reaction is generally so high as 15 to 20 MPaG, and desulfization and also denitrification are insufficient. In addition, depending on a kind of the heavy oil, deactivation of the catalyst occurs when a conversion is increased, which requires frequent withdrawal of the catalyst from the reactor and frequent supply of new catalyst into the reactor. Thus, the reactor is operated while suppressing a conversion to about 50 to 60 %.

As a technique which overcomes the above mentioned problems, there is a process wherein a petroleum heavy oil is supplied together with a cheap and disposable iron based catalyst and a recycled heavy fraction of a reaction product to a suspended bed (or a slurry bed) reactor in which hydrocracking is carried out so as to achieve a high conversion of not smaller than 90 %. In this process, as far as an activity of the used iron based catalyst is not too bad,

such high conversion is possible regardless a kind of the heavy oil when a reaction pressure is so high as not smaller than 15 MPa under the conditions of a temperature of about 450°C, a reaction time in the range between 60 minutes and 90 minutes, and a flow rate of a recycled heavy residue (+525°C) in the range between 0 % by mass and 50 % by mass (which is a ratio of the residue to a supplied petroleum heavy oil as a starting material). Such process (which is also referred to as a hydrocracking process in the suspended bed reactor wherein the iron based catalyst is used) is described in, for example, Japanese Patent Kokai Publication No. 2001-89772.

However, the above process (the hydrocracking process in the suspended bed reactor wherein the iron based catalyst is used) employs the high operation pressure, which increases a larger capital investment than that of the above mentioned thermal cracking process, and therefore it is important to lower the reaction pressure in the hydrocracking process in the suspended bed reactor wherein the iron based catalyst is used. In fact, it is possible to achieve so high conversion of not lower than 90 % while using the iron based catalyst such as a natural limonite iron ore which is cheap and highly active under the conditions of in a low reaction pressure (for example, 10 MPa) and the above mentioned reaction temperature,

reaction time, the ratio of the recycled heavy residue. Depending on a kind of the heavy oil (for example, in the case of a heavy oil which contains asphaltenes having a condensed ring numbers of not smaller than 13), a yield of coke during the hydrocracking step (which is also referred to as Toluene Insoluble (which may be referred to as "TI" hereinafter)) is large, so that recycling of the heavy residue of the reaction product (which may be referred to as "bottom recycling") increases a concentration of TI in the heavy residue (+525°C) to be recycled. In this case, since TI has almost no cracked reactivity, cracked activity of the recycled heavy residue is also decreased, so that no effect of the bottom recycling is provided, which leads to the conversion reduction as well as the oil yield reduction.

In order to suppress the TI yield, increasing the reaction pressure is effective, but it is uneconomical. Therefore, when the low reaction pressure is intended, selective removal of TI to the outside of the system (which is also referred to as "selective TI removal") is required in order to keep the concentration of TI low in the recycled heavy residue even though the yield of TI is increased under the low reaction pressure.

As a method of the selective removal of TI, there is a solid-liquid separation process of a gravity settling method with solvent addition in which process a light solvent is

added to the heavy reaction product which contains the heavy residue (comprising solid materials) to have a mixture, the mixture is charged in a settler (i.e. a separation vessel of the gravity settling type for solid-liquid separation) and an overflow comprising a material which is dissolved in the light solvent and an underflow comprising a material which is insoluble in the light solvent are withdrawn from the settler. In such solid-liquid separation process, generally a naphtha corresponding material which is light is used as the solvent and the settler is operated at a temperature of 200°C or higher, and therefore a pressure is required which is not lower than 1-2 MPa so as to keep the liquid phase in the settler, and also the solvent has to be recovered from both of the overflow and the underflow, which readily increases the cost for the separation.

When a heavy oil which causes a high TI yield is processed, a lower-cost selective TI removal process (e.g. solid-liquid separation process) is desired in order to be more economical.

If the selective TI removal becomes possible without using the above mentioned light solvent (i.e. with a solid-liquid separation process with non-solvent addition), the above problems are overcome, which, in turn, results in the lower cost.

SUMMARY OF THE INVENTION

Considering the above mentioned situation, it is an object of the present invention to omit the addition of the light solvent upon the selective TI removal during the solid-liquid separation in the hydrocracking process in which the suspended bed reactor of the iron based catalyst is used. In other words, the present invention is to provide a hydrocracking process of a petroleum heavy oil which contains a heavy metal, in which process,

the petroleum heavy oil is supplied to a suspended bed reactor and hydrocracked therein in the presence of an iron based catalyst,

a liquid phase stream comprising a heavy reaction product and TI is obtained from a reaction product of such hydrocracking through gas-liquid separation,

the liquid phase stream is subjected to solid-liquid separation so as to remove TI selectively, and then recycled to the suspended bed reactor, and

upon such selective removal of TI, no light solvent is added.

The present inventors have intensively studied so as to achieve the above object, and completed the present invention which will be described below.

The present invention provides a hydrocracking process of a petroleum heavy oil which contains a heavy

metal, wherein for such hydrocracking, a suspended bed reactor is used while an iron based catalyst are used, and the following steps (1) to (4) are carried out:

(1) a gas-liquid separation step operated at a high pressure (i.e. high pressure gas-liquid separation step) wherein a reaction product from the suspended bed reactor is divided into a gas phase stream and a liquid phase stream containing a solid component in a high pressure gas-liquid separator under the conditions of a pressure which is substantially the same as that of the suspended bed reactor and a temperature in the range between 200°C and 350°C;

(2) a gas-liquid separation step operated at a low pressure (i.e. low pressure gas-liquid separation step) wherein the liquid phase stream obtained in the above mentioned high pressure gas-liquid separation step is supplied to a low pressure gas-liquid separator and divided into a gas phase stream and a liquid phase stream containing a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C;

(3) a solid-liquid separation step wherein the liquid phase stream obtained in the above mentioned low pressure gas-liquid separation step is supplied to a solid-liquid separator of a gravity settling type (settler) so as to settle

a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, whereby a stream of an upper layer in the settler is withdrawn from an upper part of the settler while a stream containing the solid component and an oil component is withdrawn from an lower part of the settler; and

(4) a recycling step wherein a portion or a whole of the stream from the upper part of the settler obtained in the above mentioned solid-liquid separation step is recycled to the suspended bed reactor.

In one embodiment of the hydrocracking process according to the present invention, reaction conditions of the hydrocracking in the suspended bed reactor are a reaction pressure in the range between 6 MPaG and 14 MPaG, a temperature in the range between 430°C and 450°C, and a reaction time in the range between 30 minutes and 120 minutes.

In one embodiment of the hydrocracking process according to the present invention, the iron based catalyst for the hydrocracking is a limonite iron ore catalyst having an average particle diameter of not larger than 2 μm which is produced with mechanically pulverized in a petroleum based solvent, and an amount of the catalyst added for the hydrocracking is in the range of 0.3 % by mass and 2 % by

mass relative to an amount of the petroleum heavy oil which is supplied to the suspended bed reactor.

In one embodiment of the hydrocracking process according to the present invention, the temperature condition of the high pressure gas-liquid separation step is in the range between 250°C and 320°C.

In one embodiment of the hydrocracking process according to the present invention, the pressure condition is in the range between 0.3 MPaG and 0.5 MPaG and the temperature condition is in the range between 245°C and 315°C in the low pressure gas-liquid separation step, and the pressure condition is in the range between 0.3 MPaG and 0.5 MPaG and the temperature condition is in the range between 245°C and 315°C in the solid-liquid separation step.

In one embodiment of the hydrocracking process according to the present invention, an amount of the stream to be recycled to the suspended bed reactor is such that an amount of a heavy oil component having a boiling point of not lower than 525°C in said stream is in the range of 10 % by mass and 100 % by mass relative to an amount of the petroleum heavy oil which is supplied to the suspended bed reactor.

According to the hydrocracking process according to the present invention, no addition of a light solvent is

required upon the selective TI removal by means of the solid-liquid separation in the hydrocracking process which uses the suspended bed reactor of the iron based catalyst. That is, in the hydrocracking process of the petroleum heavy oil which contains the heavy metal(s),

5 the petroleum heavy oil is supplied to the suspended bed reactor and hydrocracked in the presence of the iron based catalyst,

the liquid stream comprising the heavy reaction product and TI is obtained through the gas-liquid separation from the reaction product of hydrocracking,

10 the liquid stream is subjected to the solid-liquid separation so as to remove TI (coke) selectively and then recycled to the suspended bed reactor, and

upon such selective removal of TI, no light solvent is added.

In another aspect, the present invention provides a
15 hydrocracking process of a petroleum heavy oil which contains a heavy metal, wherein for such hydrocracking, a suspended bed reactor is used as a reactor and an iron based catalyst is used as a catalyst, wherein the iron based catalyst has an average particle diameter of not larger than 2 μm , which process comprises: (1) a high
20 pressure gas-liquid separation step wherein a reaction product from the suspended bed reactor is divided into a gas phase stream and a liquid phase stream containing a solid component in a high pressure gas-liquid separator under the conditions of a pressure which is substantially the same as that of the suspended bed reactor and a
25 temperature in the range between 200°C and 350°C; (2) a low

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pressure gas-liquid separation step wherein the liquid phase stream obtained in the high pressure gas- liquid separation step is supplied to a low pressure gas-liquid separator and divided into a gas phase stream and a liquid phase stream containing a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C; (3) a solid-liquid separation step wherein the liquid phase stream obtained in the low pressure gas-liquid separation step is supplied to a solid-liquid separator of a gravity settling type, wherein said solid-liquid separator acts as a settler so as to settle a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, whereby a stream of an upper layer in the settler is withdrawn from an upper part of the settler while a stream containing the solid component and an oil component is withdrawn from a lower part of the settler; and (4) a recycling step wherein a portion or a whole of the stream from the upper part of the settler obtained in the solid-liquid separation step is recycled to the suspended bed reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a flow sheet of one embodiment of the hydrocracking process of the petroleum heavy oil according to the present invention.

Fig. 2 shows a flow sheet of other embodiment of the hydrocracking process of the petroleum heavy oil according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a hydrocracking process of a petroleum heavy oil which contains a heavy metal(s), wherein for such hydrocracking, a suspended bed reactor is used as a reactor and an iron based catalyst is used as a catalyst, and it is characterized by the following steps (1) to (4):

(1) a gas-liquid separation step at a high pressure (i.e. high pressure gas-liquid separation step) wherein a reaction product from the suspended bed reactor is divided into a gas phase stream and a liquid phase stream containing a solid component in a high pressure gas-liquid separator under the conditions of a pressure which is substantially the same as that of the suspended bed reactor and a temperature in the range between 200°C and 350°C;

(2) a gas-liquid separation step at a low pressure (i.e. low pressure gas-liquid separation step) wherein the liquid phase stream obtained in the above mentioned high pressure gas-liquid separation step is supplied to a low pressure gas-liquid separator and divided into a gas phase stream and a liquid phase stream containing a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C;

(3) a solid-liquid separation step wherein the liquid

phase stream obtained in the above mentioned low pressure gas-liquid separation step is supplied to a solid-liquid separator (settler) so as to settle a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, whereby a stream of an upper layer in the settler is withdrawn from an upper part of the settler while a stream containing the solid component and an oil component is withdrawn from an lower part of the settler; and

(4) a recycling step wherein a portion or a whole of the stream from the upper part of the settler obtained in the solid-liquid separation step is recycled to the suspended bed reactor.

In the above mentioned high pressure gas-liquid separation step (1), the reaction product produced by hydrocracking in the suspended bed reactor is supplied to the high pressure gas-liquid separator where the reaction product is separated into the gas phase stream and the liquid phase stream which contains the solid component under the conditions of a pressure which is substantially the same as that of the suspended bed reactor and a temperature in the range between 200°C and 350°C. Thus separated liquid phase stream contains a heavy oil component (i.e. heavy reaction product) and a solid

component (such as coke, and the catalyst), and it further contains a light oil component. It is noted that the heavy oil component is an oil component having a boiling point of not lower than 525°C, and the light oil component is an oil component which is other than said heavy oil component and thus has a boiling point which is lower than that of said heavy oil component.

Assuming that an amount of the light oil component in the liquid phase stream is A1, an amount of the light oil component in the reaction product is A0, and an amount of the light oil component in the gas phase stream is A2, $A1=A0-A2$. That is, a portion (having a lower boiling point) of the light oil component in the reaction product is contained in the gas phase stream, and its balance (having a higher boiling point) is contained in the liquid phase steam. The amount of the light oil component in the liquid phase steam (A1) is larger than that in the case of the prior art hydrocracking process which uses the iron based catalyst in the suspended bed reactor (which process is also referred to as "the prior process"). Namely, the liquid phase stream contains a rather larger amount of the light oil component. This is because the temperature upon the above mentioned high pressure gas-liquid separation is in the range between 200°C and 350°C which is lower than that of the prior process.

In the above mentioned low pressure gas-liquid separation step (2), the liquid phase stream obtained in the above mentioned high pressure gas-liquid separation step is supplied to the low pressure gas-liquid separator and
5 divided into a gas phase stream and a liquid phase stream containing a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C. Thus separated liquid phase stream contains the heavy oil
10 component (i.e. heavy reaction product), and the solid component (such as coke, and the catalyst) and it further contains the light oil component. It is noted that such liquid phase stream is in the state wherein a portion of the heavy oil component (the heavy reaction product) is
15 dissolved in the light oil component into which the solid component is mixed.

Assuming that an amount of the light oil component in the above mentioned liquid phase stream (i.e. the liquid phase stream separated in the low pressure gas-liquid
20 separator) is B1, an amount of the light oil component separated in the high pressure gas-liquid separator is B0, and an amount of the light oil component in the above mentioned gas phase stream (i.e. the gas phase stream separated in the low pressure gas-liquid separator) is B2,
25 $B1 = B0 - B2 = A1 - B2$. That is, a portion (having a lower boiling

point) of the light oil component in the liquid phase stream separated in the high pressure gas-liquid separation step is contained in the gas phase stream, and its balance (having a higher boiling point) is contained in the liquid phase steam. The amount of the light oil component in the liquid phase steam (B1) is larger than in the prior art process, and a rather larger amount of the light oil component is contained in the liquid phase stream. This is because the amount of the light oil component (A1) which is separated in the high pressure gas-liquid separation step is larger than that of the prior process. The amount of the light oil component in the liquid phase steam (B1) is sufficient to selectively remove T1 (coke) with no addition of a light solvent in the solid-liquid separation step.

15 In the above mentioned solid-liquid separation step (3), the liquid phase stream obtained in the above mentioned low pressure gas-liquid separation step is supplied to the settler so as to settle the solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, whereby the stream of an upper layer in the settler is withdrawn from the upper part of the separator while the stream containing the solid component and the oil component is withdrawn from the lower part of the separator. It is noted that since the liquid phase steam

supplied to the settler is already (i.e. at the time before
being supplied to the solid-liquid separator) in the state
wherein a portion of the heavy oil component (the heavy
reaction product) is dissolved in the light oil component
5 into which the solid component (the coke and the catalyst)
is mixed, the selective TI removal is possible without any
addition of a solvent into the liquid phase stream. That is,
when the liquid phase stream is supplied to the settler, the
solid content (the coke and the catalyst) settles without any
10 solvent addition, so that the selective TI removal is carried
out.

The stream thus withdrawn from the upper part of the
settler contains the rest of the heavy oil component (i.e.
heavy reaction product), and the light oil component, and it
15 is in the state wherein the rest of the heavy oil component
(the heavy reaction product) is dissolved in the light oil
component. On the other hand, the stream thus withdrawn
from the lower part of the settler contains the solid content
(the coke and the catalyst) and the oil component, and it is
20 in a slurry state wherein the solid content is mixed in the
oil component.

Thus, TI is selectively removed. That is, without
addition of any light solvent upon the selective TI removal
by the solid-liquid separation of the gravity settling, namely,
25 by solvent non-addition solid-liquid separation, TI is able to

be removed.

The reason why the selective TI removal is possible without any addition of a light solvent is that the liquid phase stream separated in the low pressure gas-liquid separation step contains a rather large amount of the light oil component, to which a portion of the heavy oil component (heavy reaction product) is dissolved to be the oil component, into which the rest of the heavy oil component (i.e. the coke and the catalyst) is mixed. In other words, the liquid phase stream to be supplied to the settler is already (i.e. at the time prior to being supplied to the settler) in such mixed state as described above, so that no additional dissolution of the heavy oil component (heavy reaction product) is necessary, which omits the addition of the light solvent which would be necessary for such additional dissolution.

In the above mentioned recycling step (4), a portion or a whole of the stream from the upper part of the settler in the solid-liquid separation step is recycled to the suspended bed reactor. The recycled stream is hydrocracked in the suspended bed reactor so that the heavy oil component (heavy reaction product) contained in the stream is converted to a material comprising a light oil component.

As described above, the hydrocracking process

according to the present invention allows the selective TI removal by the solid-liquid separation of the gravity settling with adding no light solvent upon such removal, and therefore a pressure upon the solid-liquid separation does not has to be elevated, and may be lowered to a pressure in the range between normal pressure and 1 MPaG, and also no light solvent recovery is required. That is, when a light solvent is added, a pressure in the range between 1 MPaG and 2 MPaG is required so as to keep a liquid phase in the settler, and also the solvent used has to be recovered from the overflow stream and the underflow stream, which is costly. On the other hand, in the hydrocracking process of the petroleum heavy oil according to the present invention, the pressure may be lowered to a pressure in the range between normal pressure and 1 MPaG because no light solvent is required to be added and the above described solvent recovery is not required, which allows the cost reduction.

In the above mentioned high pressure gas-liquid separation step (1), the reasons why the temperature in the range between 200°C and 350°C is selected are as follows:

When the temperature is higher than 350°C, an amount of the light oil component in the liquid phase stream obtained through the separation (A1) is decreased, which in turn decreases an amount of the light oil component in the

liquid phase stream obtained through the separation in the low pressure gas-liquid separation step (B1) so that it is difficult to ensure an amount of the light oil component which is sufficient to ensure the selective TI removal without the addition of the light solvent in the solid-liquid separation step. When the temperature is lower than 200°C, the temperature of the low pressure gas-liquid separator is lower than that of the high pressure gas-liquid separator by several degrees centigrade, which means that the solid-liquid separation is carried out maximally at a temperature of about 200°C. The solid-liquid separation at a temperature lower than 200°C involves a higher viscosity of a liquid, which adversely affects the performance of the solid-liquid separation. Therefore, the temperature in the range between 200°C and 350°C is selected in the high pressure gas-liquid separation step.

Further, in the above mentioned high pressure gas-liquid separation step (1), the pressure is selected to be substantially the same as that of the suspended bed reactor. Such pressure corresponds a pressure when the reaction product is supplied from the suspended bed reactor to the high pressure gas-liquid separator as it is, and it is possible that the pressure is the same as or lower than that of the suspended bed reactor. In order to cover such possible pressures also, the expression "substantially the

same as" is used. That is, the pressure which is substantially the same as that of the suspended bed reactor is not limited to only the pressure of the suspended bed reactor, and includes also a pressure which is decreased
5 spontaneously from the pressure of the suspended bed reactor.

In the above mentioned low pressure gas-liquid separation step (2), the conditions of a pressure in the range between normal pressure and 1 MPaG and a
10 temperature in the range between 190°C and 340°C are employed. It is noted that such pressure is expressed as a gauge pressure. For example, 1 MPaG corresponds to an absolute pressure of 1.1 MPa, and the normal pressure corresponds to 0 MPaG as a gauge pressure and also to
15 0.101 MPa as an absolute pressure. It is noted that since 1 MPaG = 1×10^6 Pa and 9.80665×10^4 Pa = 1 kgf/cm² (that is, 0.980665×10^5 Pa = 1 kgf/cm²), 0.980665 MPa = 10 kgf/cm². Thus, the above mentioned 1 MPaG is $10/0.980665$ kgf/cm², which is about 10 kgf/cm². The above
20 mentioned normal pressure is 0.101 MPa (normal pressure = 1 atm = 1.033 kgf/cm² = 1.033×0.0980665 MPa = 0.101 MPa).

In the above mentioned solid-liquid separation step (3), the conditions of a pressure in the range between normal
25 pressure and 1 MPaG and a temperature in the range

between 190°C and 340°C are employed. The reasons why the pressure in the range between the normal pressure and 1 MPaG is employed are as follows:

As described above, the hydrocracking process of the petroleum heavy oil according to the present invention allows the selective TI removal without the addition of the light solvent, which in turn deletes the necessity of increase of the operation pressure in the solid-liquid separation for the purpose of the selective TI removal, so that the pressure may be lowered to a pressure in the range between the normal pressure and 1 MPaG. Therefore, the pressure in the range between the normal pressure and 1 MPaG is employed in the solid-liquid separation step (3), which leads to the cost reduction.

In the hydrocracking process of the petroleum heavy oil according to the present invention, the reaction conditions in the suspended bed reactor is not particularly limited, and for example the following conditions may be employed:

reaction pressure: 6 to 14 MPaG
reaction temperature: 430 to 450°C
reaction period: 30 to 120 minutes

As to the iron based catalyst, the followings are desirable: limonite iron ore catalyst is used in the form of particles of which average diameter is not larger than 2 μm ;

such catalyst is produced by being mechanically pulverized in a petroleum solvent; and an amount of the catalyst to be added is in the range of 0.3 % by mass of iron and 2% by mass of iron relative to an amount of the petroleum heavy oil to be supplied to the reactor. The reason why such limonite iron ore catalyst is preferably used is that it is more active than the other iron based catalyst such as Fe_2O_3 (hematite), FeS_2 (pyrite), FeSO_4 (iron sulfate) or the like, and that it is a cheap catalyst which is naturally mined. When the added amount is smaller than 0.3 % by mass, the formation of coke sharply increases. When the added amount is larger than 2 % by mass, an oil yield hardly increases while the cost increases.

It is noted that the above mentioned average diameter of the catalyst particles is measured using an apparatus for particle size distribution measurement using laser diffraction. Concretely, the iron based catalyst particles in a petroleum solvent are dispersed in ethanol, and a particle diameter distribution curve (i.e. a curve of diameter vs. accumulative weight percents) is obtained by using such apparatus. Based on the obtained curve, a diameter at fifty percents (so called Dp50) is obtained as the average diameter.

In the high pressure gas-liquid separation step, the temperature therein is desirably in the range between

250°C and 320°C. Such temperature condition leads to a larger amount of the light oil component (A1) in the liquid phase stream obtained by the separation, which in turn increases an amount of the light oil component (B1) in the liquid phase stream obtained by the low pressure gas-liquid separation, so that an amount of the light oil component is easily ensured which amount is sufficient to carry out the selective TI removal without the addition of the light solvent in the solid-liquid separation step, whereby the selective TI removal without the addition of the solvent is more easily ensured.

In one embodiment of the hydrocracking process according to the present invention, the low pressure gas-liquid separation step desirably employs the conditions of a pressure in the range between 0.3 MPaG and 0.5 MPaG and a temperature in the range between 245°C and 315°C while the solid-liquid separation step desirably employs the conditions of a pressure in the range between 0.3 MPaG and 0.5 MPaG and a temperature in the range between 245°C and 315°C. The reasons why the above mentioned conditions are preferably selected are as follows:

As described above, it is described that the temperature of the high pressure gas-liquid separation step is desirably in the range between 250°C and 320°C. When the liquid phase stream of such high pressure gas-liquid

separation is supplied to the low pressure separation step at a pressure in the range between 0.3 MPaG and 0.5 MPaG, the stream flashes into a gas phase stream and a liquid phase stream under such low pressure, so that the
5 temperature in the low pressure gas-liquid separation step becomes lower than that of the high pressure gas-liquid separation step, and such lower temperature is in the range between 245°C and 315°C. At a pressure in the pressure range between 0.5 MPaG and 1 MPaG in the low pressure
10 gas-liquid separation step (LPS), an amount (B2) of the light oil component which is contained in the liquid phase stream from the high pressure gas-liquid separation step and which is transferred to the gas phase stream is small, so that an amount of B1 is kept large. However, such
15 pressure in the above mentioned range is rather high, which leads to a high cost of the apparatus. On the other hand, a pressure in the range between the normal pressure and 0.3 MPaG in the LPS leads to the cheaper cost of the apparatus, but an amount of B2 is rather increased (that is, an amount
20 of B1 is decreased), which adversely affects the performance of the solid-liquid separation a little. The pressure in the range between 0.3 MPaG and 0.5 MPaG in the LPS keeps an amount of B1 relatively large, and also leads to a good performance of the solid-liquid separation
25 and further to the cost reduction of the apparatus, which

means that the pressure in the range between 0.3 MPaG and 0.5 MPaG in the LPS is a desirable condition.

It is desirable that an amount of the stream to be recycled to the suspended bed reactor in the recycling step is such that an amount of the heavy oil component having a boiling point of not lower than 525°C is in the range between 10 % by mass and 100 % by mass relative to an amount of the petroleum heavy oil which is supplied to the suspended bed reactor. When the amount of the stream to be recycled is smaller than 10 % by mass, an oil yield hardly increases, so that no effect of the bottom recycling is expected. On the other hand, when the amount of the stream to be recycled is larger than 100 % by mass, the oil yield drastically increases when compared with the amount of smaller than 10 % by mass, but an increase rate of the oil yield is smaller than that in the case wherein amount of the stream to be recycled in the range between 10 % by mass and 100 % by mass, and such smaller increase rate means a worse efficiency of the bottom recycling.

A flow sheet of the hydrocracking process of the petroleum heavy oil according to the present invention is shown in Figs. 1 and 2, wherein the reference numbers indicate the following elements:

1: slurry preparation vessel,

2: preheater,

- 3: suspended bed reactor,
- 4: high pressure gas-liquid separator,
- 5: high pressure/low temperature gas-liquid separator,
- 6: distillation column 1,
- 5 7: gas purification step,
- 8: low pressure gas-liquid separator,
- 9: settler,
- 10: distillation column 2

10 In the above elements, the suspended bed reactor 3 corresponds to an example of the suspended bed reactor in the present invention, the high pressure gas-liquid separator 4 corresponds to an example of the high pressure gas-liquid separator in the present invention, the low pressure gas-liquid separator 8 corresponds to an example of the low pressure gas-liquid separator in the present invention, and the settler 9 corresponds to an example of the settler of the solid-liquid separation in the present invention. In the process flow sheet shown in Fig. 1, the settler is for a batch operation. In the process flow sheet shown in Fig. 2, the settler is for a continuous operation.

20 It is noted that the heavy oil component in the heavy reaction product means an oil component having a boiling point of not lower than 525°C, and the light oil component therein means an oil component which is other than the heavy oil component and of which boiling point is lower

25

than that of the heavy oil component.

EXAMPLE

5 An example of the present invention and also a comparative example will be explained below. It is noted that the present invention is not limited to the example, and also that any modification in the example is possible within the concept of the present invention and such modification would be covered by the scope of the accompanying claims.

10

Example 1

The hydrocracking process of the petroleum heavy oil which contains heavy metals was carried out in a plant of which flow sheet is as shown in Fig. 1, which will be
15 described below in detail.

The petroleum heavy oil was supplied to the suspended bed reactor together with the iron based catalyst so as to carry out the hydrocracking reaction. As the heavy oil, a vacuum residue (which is referred to as also "VR")
20 was used. As the iron based catalyst, limonite iron ore was used. An amount of the catalyst supplied was 1 % by mass of iron relative to an amount of the heavy oil to be supplied. Further, sulfur was supplied as a co-catalyst. A mol ratio of the co-catalyst to an amount of iron of the catalyst was
25 1.2. The suspended bed reactor was operated under the

following conditions:

reaction pressure: 10 MPa

reaction temperature: 450°C

reaction time: 90 minutes

5 recycled residue (heavy oil component, +525°C):

50 % by mass of VR

The reaction product obtained in the above suspended
bed reactor was supplied to the high pressure gas-liquid
separator where the high pressure gas-liquid separation
10 step was carried out so as to obtain a gas phase stream
and a liquid phase stream which comprises a solid
component. The high pressure gas-liquid separator was
operated under the conditions of a pressure of 10 MPa
which is substantially the same as that of the suspended
15 bed reactor and a temperature of 310°C.

The liquid phase stream obtained in the above
mentioned high pressure gas-liquid separation step was
supplied to the low pressure gas-liquid separator where the
low pressure gas-liquid separation step was carried out so
20 as to obtain a gas phase stream and a liquid phase stream
which comprises a solid component. The low pressure gas-
liquid separator was operated under the conditions of a
pressure of 0.5 MPa and a temperature of 300°C.

The liquid phase stream obtained in the above low
25 pressure gas-liquid separator was supplied to the solid-

liquid separator (i.e. the settler), and then left standing for 30 minutes under a pressure of 0.5 MPa at a temperature of 300°C. Thereafter, the upper layer in the vessel was withdrawn from the settler through an inserted tube while the remaining lower layer was withdrawn from the bottom of the vessel. It is noted that the tube was inserted into the settler from a top thereof such that its port end was located at an 85 % level of the height of the settler from its bottom. In this way, the solid-liquid separation was carried out.

The upper layer and the lower layer which were withdrawn from the settler as described above had compositions shown in the following Table 1:

Table 1

component	composition of upper layer (wt %)	composition of lower layer (wt %)
Oil (C5-525°C)	62.24	50.94
TS component ¹⁾	31.94	3.42
TI component ²⁾	4.86	26.76
catalyst	0.96	18.87

¹⁾ TS component: component of which average boiling point is not lower than 525°C and which is soluble in toluene

²⁾ TI component: component of which average boiling point is not lower than 525°C and which is insoluble in toluene

It is seen from Table 1 that TI component and the catalyst are concentrated in the lower layer while amounts of them in the upper layer in the settler are small.

The recycling step was carried out by recycling to the suspended bed reactor a portion of the upper layer which was withdrawn from the settler in the solid-liquid separation step.

As a result, a conversion of 91 %, a residue (+525°C) yield of 7.3 % by mass relative to a VR amount and an oil yield of 85 % by mass relative to a VR amount were achieved. The conversion was calculated according to the following equation (1):

$$\text{Conversion (\%)} = 100 \times (A-B)/A \quad (1)$$

wherein A is a weight % of a +525°C component in the feed VR, and B is a yield of the produced residue (+525°C).

It is noted that a distillate composition of the feed VR had a composition shown in the following Table 2:

Table 2

composition of distillate in feed VR (wt %)				
-171°C	171°C-232°C	232°C-343°C	343°C-525°C	+525°C
-	-	-	16.4	83.6

20

Comparative Example 1

The hydrocracking process was carried out using the

same petroleum heavy oil, the same iron based catalyst, and the same suspended bed reactor as in Example 1 under the same conditions also as in Example 1. The reaction product was supplied to the high pressure gas-liquid separator in which the pressure was 10 MPaG which was the same as that of the suspended bed reactor and the temperature was 370°C. The liquid stream obtained by the high pressure gas-liquid separator was supplied to the low pressure gas-liquid separator wherein the low pressure gas-liquid separation was carried out under the same conditions as those in Example 1.

That is, the hydrocracking step, the high pressure gas-liquid separation step and the low pressure gas-liquid separation step were carried out under the same conditions as those in Example 1 except that the temperature in the high pressure gas-liquid separator was of a higher (i.e. 370°C) than that of Example 1 (i.e. 310°C).

The liquid phase stream obtained in the above mentioned low pressure gas-liquid separator was supplied to the settler, and then left standing for 60 minutes under a pressure of 0.5 MPa at a temperature of 300°C. Thereafter, as in Example 1, the upper layer in the vessel was withdrawn from the settler while the remaining lower layer was withdrawn from the bottom of the vessel. That is, the solid-liquid separation was carried out under the same

conditions as those in Example 1 except that the settling time was longer (60 minutes) than that of Example 1 (30 minutes).

The upper layer and the lower layer which were withdrawn from the settler as described above had compositions shown in the following Table 3:

Table 3

component	composition of upper layer (wt %)	composition of lower layer (wt %)
Oil (C5-525°C)	53.05	49.95
TS component ¹⁾	32.64	26.10
TI component ²⁾	11.28	19.70
catalyst	3.03	4.25

¹⁾ TS component: component of which average boiling point is not lower than 525°C and which is soluble in toluene

²⁾ TI component: component of which average boiling point is not lower than 525°C and which is insoluble in toluene

It is seen from Table 3 that when compared with Example 1, contents of TI component and the catalyst are very small in the lower layer while amounts of them in the upper layer in the settler are considerably large.

The recycling step was carried out by recycling to the

suspended bed reactor a portion of the upper layer which was withdrawn from the settler in the solid-liquid separation step.

As a result, a conversion of 81 %, a residue (+525°C) yield of 15.6 % by mass relative to a VR amount and an oil yield of 75.1 % by mass relative to a VR amount were achieved. The conversion was calculated according to the above mentioned equation (1).

As described above, in Comparative Example 1, TI and the catalyst were not so sufficiently concentrated in the lower layer in the solid-liquid separation step while the amounts of them in the upper layer are large even with the longer settling time (60 minutes) in the settler, so that upon recycling the upper layer to the hydrocracking step, the conversion is low, and the yield of the residue (+525°C) is large, which in turn decreases the oil yield.

To the contrary, in Example 1, TI and the catalyst were highly concentrated in the lower layer in the solid-liquid separation step while the amounts of them in the upper layer are considerably small even with the shorter settling time (30 minutes) in the settler, so that upon recycling the upper layer to the hydrocracking step, the conversion is greatly high, and the yield of the residue (+525°C) is very small, which in turn greatly increase the oil yield.

This is because the temperature in the high pressure gas-liquid separator is lower in Example 1 than that in Comparative Example 1, which highly improves the selective TI removal. That is, the performance of the selective TI removal is low in Comparative Example 1, and in order to improve the above mentioned conversion, residue yield and oil yield up to those as in Example 1, a light solvent has to be added in the solid-liquid separation step for the selective TI removal. However, in Example 1, the highly improved selective TI removal is possible even without any addition of such light solvent.

INDUSTRIAL APPLICABILITY OF THE INVENTION

The hydrocracking process of the petroleum heavy oil according to the present invention is economically preferable as the hydrocracking process of such heavy oil, because the effects as described above are provided upon hydrocracking, in the presence of the iron based catalyst, the petroleum heavy oil containing the heavy metal in the suspended bed reactor and recycling the heavy oil component of the reaction product to the reactor.

WHAT IS CLAIMED IS:

1. A hydrocracking process of a petroleum heavy oil which contains a heavy metal, wherein for such hydrocracking, a suspended bed reactor is used as a reactor and an iron based catalyst is used as a catalyst,

wherein the iron based catalyst has an average particle diameter of not larger than 2 μm ,

which process comprises:

(1) a high pressure gas-liquid separation step wherein a reaction product from the suspended bed reactor is divided into a gas phase stream and a liquid phase stream containing a solid component in a high pressure gas-liquid separator under the conditions of a pressure which is substantially the same as that of the suspended bed reactor and a temperature in the range between 200°C and 350°C;

(2) a low pressure gas-liquid separation step wherein the liquid phase stream obtained in the high pressure gas-liquid separation step is supplied to a low pressure gas-liquid separator and divided into a gas phase stream and a liquid phase stream containing a solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, wherein the solid component is the iron based catalyst having an average particle diameter of not larger than 2 μm ;

(3) a solid-liquid separation step wherein the liquid phase stream obtained in the low pressure gas-liquid separation step is supplied to a solid-liquid separator of a gravity settling type, wherein said solid-liquid separator acts as a settler so as to settle the solid component under the conditions of a pressure in the range between normal pressure and 1 MPaG and a temperature in the range between 190°C and 340°C, whereby a stream of an upper layer in the settler is withdrawn from an upper part of the settler while a stream containing the solid component and an oil component is withdrawn from a lower part of the settler; and

(4) a recycling step wherein a portion or a whole of the stream from the upper part of the settler obtained in the solid-liquid separation step is recycled to the suspended bed reactor.

2. The hydrocracking process according to claim 1 wherein reaction conditions of the hydrocracking in the suspended bed reactor are a reaction pressure in the range between 6 MPaG and 14 MPaG, a temperature in the range between 430°C and 450°C, and a reaction time in the range between 30 minutes and 120 minutes.

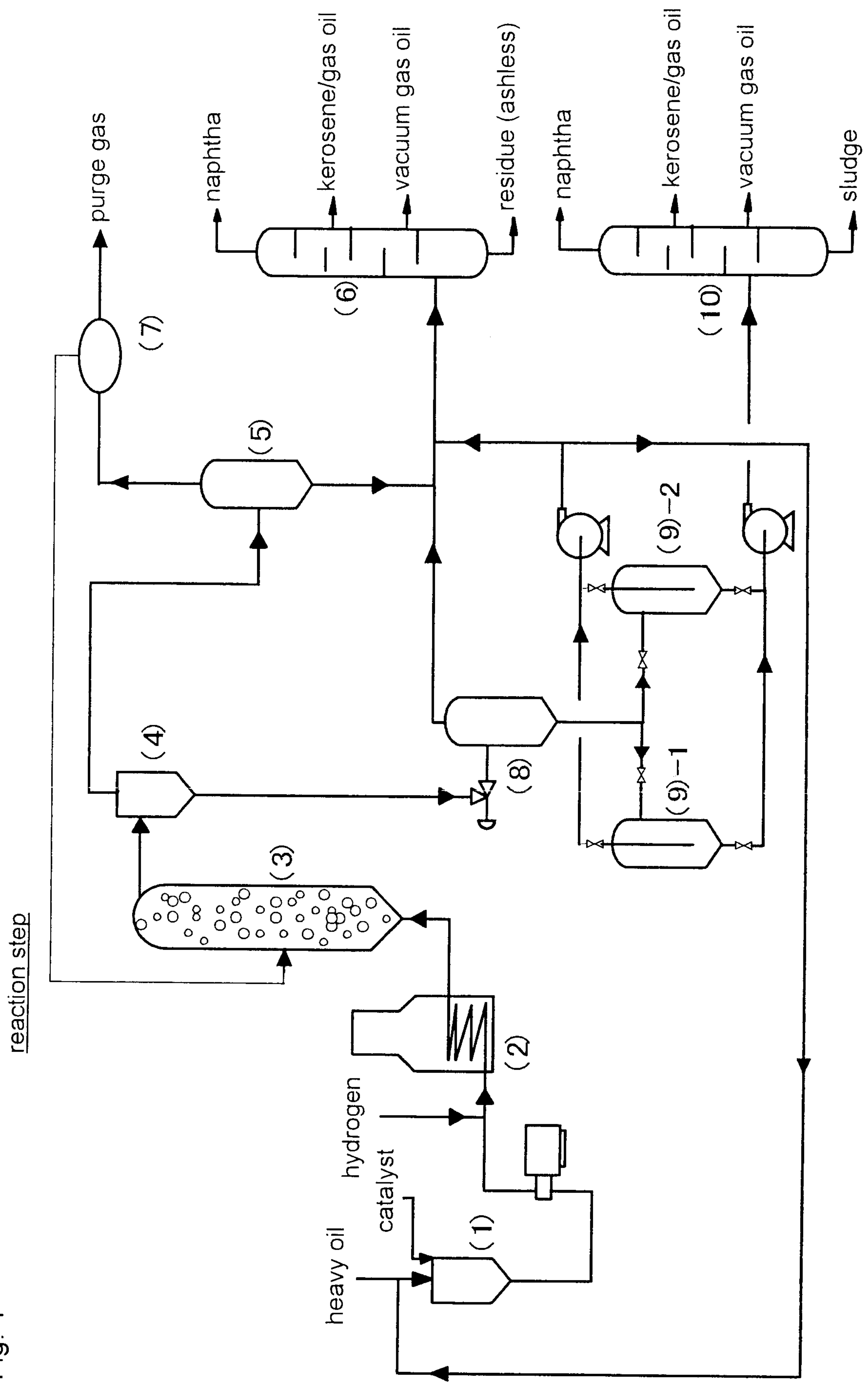
3. The hydrocracking process according to claim 1 or 2 wherein the iron based catalyst for the hydrocracking is a limonite iron ore catalyst which is produced by being mechanically pulverized in a petroleum based solvent, and an amount of the catalyst added for the hydrocracking is in the range of 0.3 % by mass of iron and 2 % by mass of iron relative to an amount of the petroleum heavy oil which is supplied to the suspended bed reactor.

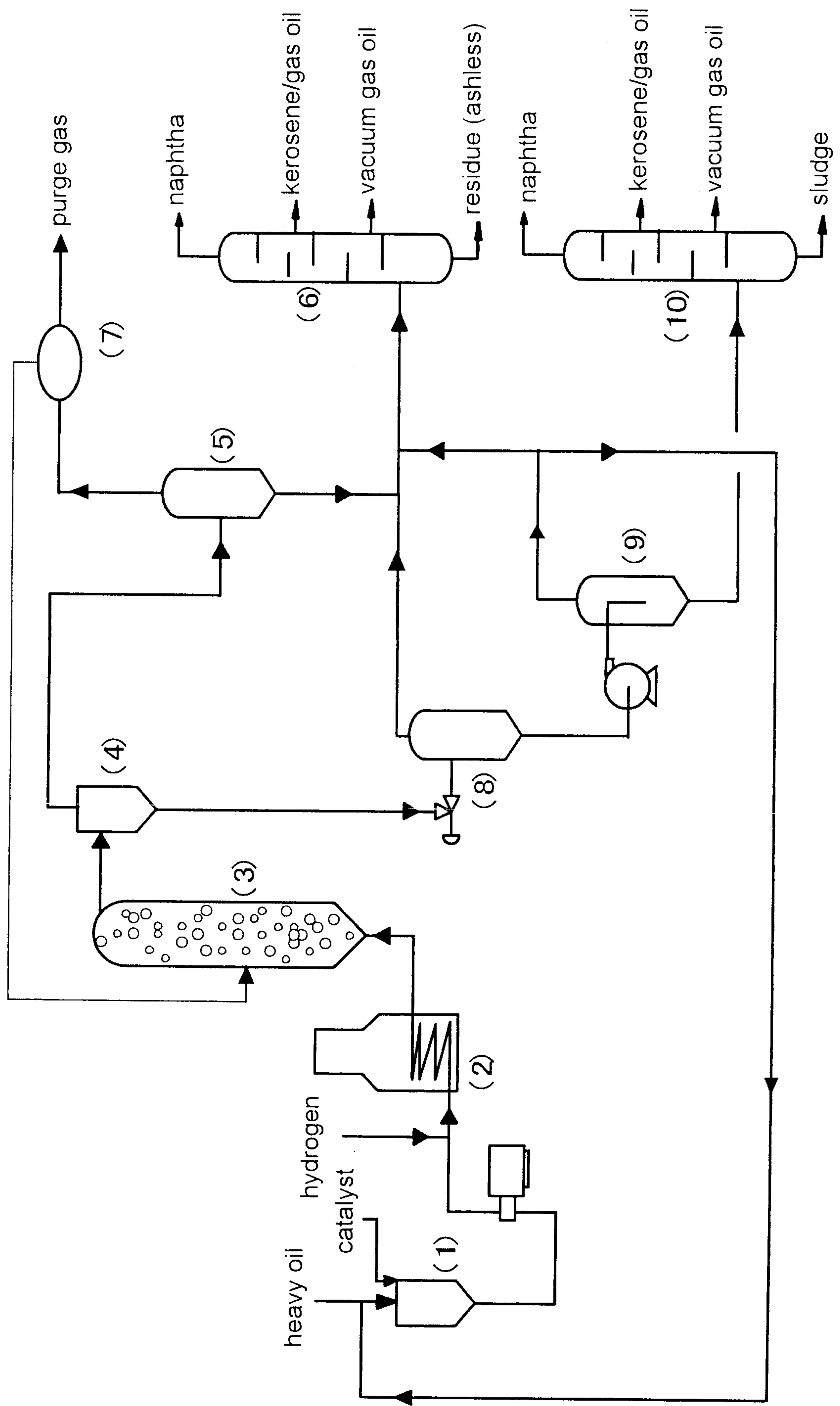
4. The hydrocracking process according to any one of claims 1 to 3 wherein the temperature condition of the high pressure gas-liquid separation step is in the range between 250°C and 320°C.

5. The hydrocracking process according to any one of claims 1 to 4 wherein the pressure condition is in the range between 0.3 MPaG and 0.5 MPaG and the temperature condition is in the range between 245°C and 315°C in the low pressure gas-liquid separation step, and the pressure condition is in the range between 0.3 MPaG and 0.5 MPaG and the temperature condition is in the range between 245°C and 315°C in the solid-liquid separation step.

6. The hydrocracking process according to any one of claims 1 to 5 wherein an amount of the stream to be recycled to the suspended bed reactor is such that an amount of a heavy oil component having a boiling point of not lower than 525°C in said stream is in the range of 10 % by mass and 100 % by mass relative to an amount of the petroleum heavy oil which is supplied to the suspended bed reactor.

Fig. 1



reaction step

reaction step

