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(54) Title: METHOD FOR HYDROCRACKING PETROLEUM HEAVY OIL

(57) Abrégé/Abstract:

Disclosed is a method for hydrocracking a petroleum heavy oil that is used to obtain a high distillate yield economically in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue. Specifically, the method comprises a reaction step of supplying a raw material slurry containing a petroleum heavy oil and a limonite ore catalyst, and a hydrogen gas to a suspended-bed reactor; and a step of hydrocracking the heavy oil under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes, wherein pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is performed during heating of the raw material slurry up to the reaction temperature: 430 to 455 °C.

ABSTRACT

Disclosed is a method for hydrocracking a petroleum heavy oil that is used to obtain a high distillate yield economically in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue. Specifically, the method comprises a reaction step of supplying a raw material slurry containing a petroleum heavy oil and a limonite ore catalyst, and a hydrogen gas to a suspended-bed reactor; and a step of hydrocracking the heavy oil under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes, wherein pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is performed during heating of the raw material slurry up to the reaction temperature: 430 to 455 °C.

METHOD FOR HYDROCRACKING PETROLEUM HEAVY OIL

Background of the Invention

1. Field of the Invention

The present invention pertains to a technical field concerning a method for hydrocracking a petroleum heavy oil. More specifically, it relates to a method for hydrocracking a petroleum heavy oil containing heavy metals, and more particularly, it pertains to a technical field concerning a method for hydrocracking a petroleum heavy oil containing heavy metals such as an atmospheric residue or a vacuum residue, and obtaining a high distillate yield.

2. Description of Related Art

There are taking place sharp changes that the increase in proportion of heavy oils in the mined crude oils and the increase in demand for light oils are proceeding simultaneously. With such a trend as a background, a heavy oil cracking technology for manufacturing a light product deficient in supply from surplus heavy oils is receiving attention. Under the situation where the decrease in limited petroleum reserves is unavoidable, the importance of the heavy oil cracking technology is increasingly being enhanced.

Up to now, a large number of methods have been proposed on thermal cracking and hydrocracking of heavy oils. However, these methods have some problems for the upgrading of a heavy

oil such as a vacuum residue. The details will be described below.

The heavy oils such as vacuum residues tend to contain considerably large amounts of nitrogen and sulfur compounds, and further contain large amounts of organic metallic impurities which are likely to be very harmful when heavy oil cracking is conducted in the presence of a catalyst. Such metallic impurities often contain nickel (Ni) and vanadium (V), and also contain other metals. The metallic impurities are chemically bonded to relatively higher polymer organic compounds such as asphaltene in a heavy oil. The presence thereof considerably inhibits the catalytic activity on the removal of nitrogen-, sulfur-, and oxygen-containing compounds, and the hydrocracking reaction of heavy organic substances.

As a process for cracking a heavy oil such as a vacuum residue without using a catalyst, a so-called coker process, which is a thermal cracking process, is known. However, this process is encountered with a problem of disposal of cokes by-produced in large quantities. In addition, the process has the following drawbacks: the reduction in yield of the distillate (oil) is unavoidable due to an increase in amount of gases caused by excess cracking; and further, the distillate is rich in aromatic and olefin compounds, and hence it is inferior in quality.

With a hydrocracking process of a fixed bed reactor system

to be carried out by filling a granular catalyst in a reactor, if the upgrading is carried out to a high degree, the cokes produced from the asphaltene and the heavy metals such as V and Ni are gradually deposited on a catalyst layer. This results in a reduction in activity of the catalyst and blocking of the catalyst layer, unfavorably making it impossible to achieve the long-term continuous operation.

With a hydrocracking process of an ebullated-bed reactor system using an extruded particle catalyst of Co-Mo system or the like, there occurs no problem of an increase in pressure drop caused by the deposition of cokes and the like due to the intense mixing conditions in the ebullated-bed reactor. Further, it is possible to draw and supply the catalyst during operation, which enables the long-term continuous operation with the catalyst activity held constant. Thus, the process has advantages over the hydrocracking process of the fixed bed reactor system. However, a mechanical problem with a pump or the like is encountered because the catalyst is circulated during the operation. Therefore, the operation is more difficult to perform with this process than with the hydrocracking process of the fixed bed reactor system. Further, the catalyst is high-priced, the reaction pressure is generally as high as 150 to 200 kg/cm², and unfavorably the desulfurization and denitrogenation of reaction products are insufficient.

Summary of the Invention

The present invention has been completed in view of such circumstances. It is therefore an object of the present invention to provide a method for hydrocracking a petroleum heavy oil capable of obtaining a high distillate (b.p. < 525°C) yield economically in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue.

In order to achieve the foregoing object, a method for hydrocracking a petroleum heavy oil in accordance with the present invention is implemented as the methods for hydrocracking a petroleum heavy oil according to a first aspect to a third aspect, which are configured as follows.

Namely, the method for hydrocracking a petroleum heavy oil according to the first aspect is a method for hydrocracking a petroleum heavy oil containing heavy metals. The method for hydrocracking a petroleum heavy oil, comprises a reaction step of supplying a raw material slurry containing a petroleum heavy oil with heavy metals, a limonite ore added as a catalyst, and elemental sulfur added as a promoter, and a hydrogen gas to a suspended-bed reactor, and hydrocracking the heavy oil under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes, characterized in that pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is performed during heating of the raw material

slurry up to a reaction temperature: 430 to 455°C (First invention).

The method for hydrocracking a petroleum heavy oil according to the second aspect is a method for hydrocracking a petroleum heavy oil containing heavy metals, comprising the steps of: supplying a raw material slurry containing the heavy oil and a limonite ore to a suspended-bed reactor; and hydrocracking the heavy oil in the reactor under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455°C, and reaction time: 30 to 180 minutes, wherein pretreating in which the raw material slurry is heated at a temperature of 320 to 420°C for 10 to 60 minutes is carried out during heating of the raw material slurry up to the reaction temperature, wherein the heating temperature in the pretreating is set at 340 to 400°C.

The method for hydrocracking a petroleum heavy oil according to the third aspect is a method for hydrocracking a petroleum heavy oil as described above, wherein the heating time in the pretreating is set at 20 to 40 minutes (Third invention).

In another aspect, the present invention provides a method for hydrocracking a petroleum heavy oil containing heavy metals, comprising the steps of: supplying a raw material slurry containing the heavy oil, a limonite ore and elemental sulfur to a suspended-bed reactor; and hydrocracking the heavy oil in the reactor under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction

temperature: 430 to 455°C, and reaction time: 30 to 180 minutes, wherein said method further comprises a pretreating step in which the raw material slurry is heated at a temperature of 320 to 420°C for 10 to 60 minutes during heating of the raw material slurry up to the reaction temperature.

Other and further objects, features and advantages of the invention will appear more fully from the following description.

Brief Description of the Drawing

FIG. 1 is a graph showing the relationship between the pretreating temperature and the distillate (oil) (b.p.: not more than 525 °C) yield in pretreating in accordance with Examples and Comparative Examples.

Detailed Description of the Preferred Embodiments

The present invention is carried out, for example, in the following manner.

To a petroleum heavy oil containing heavy metals such as a vacuum residue, a limonite ore is added as a catalyst, and elemental sulfur is added as a promoter, resulting in a raw material slurry. The resulting raw material slurry is supplied to a suspended-bed reactor together with a hydrogen gas. Thus, the reaction step of hydrocracking the heavy oil is carried out under the reaction conditions of reaction pressure: 30 to 160 kg, reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes. In this step, pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is carried out during heating of the raw material slurry up to a reaction temperature of 430 to 455 °C. Thereafter, the temperature is raised to the reaction temperature of 430 to 455 °C.

The method for hydrocracking a petroleum heavy oil in accordance with the present invention is carried out in this manner. Below, the present invention will be described mainly as to its function and effect.

A method for hydrocracking a petroleum heavy oil in accordance with the present invention, basically includes a reaction step of supplying a raw material slurry containing a petroleum heavy oil with heavy metals, a limonite ore added as a catalyst, and elemental sulfur added as a promoter, and a hydrogen gas to a suspended-bed reactor, and hydrocracking the heavy oil under the reaction conditions of reaction pressure:

30 to 160 kg/cm², reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes (below, also referred to as a basic reaction step). The limonite ore has a very high catalytic activity for hydrocracking, and is a low-priced and disposable catalyst. Particularly due to this point, it is possible to obtain a distillate (below oil) with a high yield in the foregoing basic reaction step, and further the catalyst is low-priced and economically excellent. Therefore, it is possible to obtain an oil economically and with a high yield in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue.

Further, at this step, for heating the raw material slurry up to a reaction temperature of 430 to 455 °C, not simply (monotonously) the temperature is raised to a reaction temperature of 430 to 455 °C, but pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is carried out during heating. Thereafter, the temperature is raised to the reaction temperature: 430 to 455 °C. Due to this, the reactivity of hydrocracking of the heavy oil is enhanced, and therefore, it is possible to enhance the yield of the oil and to obtain a light oil with a higher yield.

The function and effect of the present invention will be described in details below.

The catalyst for hydrocracking is required to be

basically high in activity as a catalyst (to have a high capability of enhancing the hydrocracking efficiency as a catalyst), to be low-priced and readily available from the economical point of view, and to have other properties. Iron-based catalysts such as iron sulfide, iron oxide, and red mud are known in terms of being low-priced, but they are unfavorably insufficient in activity as a catalyst (below, referred to as a catalytic activity). The present inventors have conducted a close study on the effect of the iron-based catalyst species on the hydrocracking activity for a petroleum heavy oil. As a result, they have found that a limonite ore is excellent in catalytic activity for a petroleum heavy oil.

Based on such a finding, in the method for hydrocracking a petroleum heavy oil in accordance with the present invention, basically, a limonite ore is used as a catalyst for hydrocracking. Thus, the method is so configured as to include: a reaction step (basic reaction step) of adding a limonite ore as a catalyst, and adding elemental sulfur as a promoter to a petroleum heavy oil containing heavy metals, resulting in a raw material slurry, supplying the resulting the raw material slurry to a suspended-bed reactor together with a hydrogen gas, and hydrocracking the heavy oil under the reaction conditions of reaction pressure: 30 to 160 kg, reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes.

The limonite ore is, as described above, not only

excellent in catalytic activity for a petroleum heavy oil, but also a low-priced and disposable catalyst. Particularly due to this point, the reactivity of hydrocracking of a heavy oil is excellent in the basic reaction step, so that it is possible to obtain an oil with a high yield. Further, the reaction step is economically excellent because the catalyst to be used therefor is low-priced. Therefore it is possible to obtain an oil economically and with a high yield in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue.

Now, there will be explained below the reason why the reaction conditions for the basic reaction step are set as follows: reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455 °C, and reaction time: 30 to 180 minutes.

The reason for setting the reaction pressure at 30 to 160 kg/cm² is as follows. If the reaction pressure is less than 30 kg/cm² [$9.80665 \times 10^4 \text{ Pa}/(\text{kg}/\text{cm}^2) \times 30 \text{ kg}/\text{cm}^2 = 2.94 \times 10^6 \text{ Pa} = 2.94 \text{ MPa}$], the amount of coke formed increases because of the low hydrogen partial pressure. Whereas, if the reaction pressure is more than 160 kg/cm², the degree of contribution of the increase in pressure to the reaction acceleration is not remarkable, resulting in a high cost. The reason for setting the reaction temperature at 430 to 455 °C is as follows. If the reaction temperature is less than 430 °C, the hydrocracking reaction is not accelerated, so that it is difficult to produce

an oil with a high yield. Whereas, if the reaction temperature is more than 455 °C, the thermal cracking occurs more intensively, and the rate of the polycondensation reaction increases, resulting in a sharp increase in amount of coke formed. The reason for setting the reaction time at 30 to 180 minutes is as follows. If the reaction time is less than 30 minutes, it is difficult to obtain a high oil yield. Whereas, if the reaction time is more than 180 minutes, the hydrocracking reaction proceeds too far, resulting in an increase in amount of a hydrocarbon gas formed. Accordingly, not only the amount of the oil produced is reduced, but also the amount of hydrogen consumed increases more than necessary, resulting in a high cost.

With the method for hydrocracking a petroleum heavy oil in accordance with the present invention, further, for heating the raw material slurry up to a reaction temperature of 430 to 455 °C in the basic reaction step, not simply (monotonously) the temperature is raised to a reaction temperature of 430 to 455 °C, but pretreating in which the raw material slurry is heated at a temperature of 320 to 420 °C for 10 to 60 minutes is carried out during heating. Thereafter, the temperature is raised to the reaction temperature of 430 to 455 °C. Due to this, the reactivity of hydrocracking of the heavy oil is enhanced, and therefore, it is possible to enhance the oil yield and to obtain a light oil with a high yield. This is due to

the following reasons (1) to (3).

(1) Enhancement of catalytic activity due to more smooth proceeding of sulfurization of limonite ore catalyst

A limonite ore (FeOOH) catalyst starts to react with sulfur from a temperature of about $200\text{ }^{\circ}\text{C}$ to form pyrrhotite (Fe_{1-x}S). The resulting pyrrhotite exhibits a catalytic activity. At this step, a part of FeOOH forms troilite (FeS) which is considered to be low in activity.

Upon performing the foregoing pretreating, the sulfurization of the limonite ore catalyst proceeds smoothly, so that the formation of troilite (FeS) is inhibited, resulting in an increase in amount of pyrrhotite formed, and the crystal size of pyrrhotite formed decreases. Therefore, the catalytic activity is enhanced, and hence the reactivity of hydrocracking of a heavy oil is enhanced.

(2) Enhancement of reactivity due to the inhibition of the polycondensation reaction of thermally cracked radicals of a heavy oil

A part of a heavy oil starts to undergo thermal cracking from about $350\text{ }^{\circ}\text{C}$. The thermal cracking rate increases with an increase in temperature.

A hydrogen atom is donated to the radical resulting from the thermal cracking of the heavy oil (thermally cracked radical) through a catalyst, so that the hydrocracking reaction proceeds well.

If the temperature is raised to the reaction temperature of 430 to 455 °C simply (in one step) for heating the raw material slurry up to the reaction temperature, the rate at which hydrogen atoms are donated to the thermally cracked radicals cannot overtake the rate of formation of thermally cracked radicals. Accordingly, the polycondensation reaction occurs between the thermally cracked radicals. As a result, the reactivity is reduced, so that the oil yield becomes low.

In contrast, upon performing the foregoing pretreating, the formation of radicals resulting from thermal cracking is inhibited. Accordingly, sufficient hydrogen atom donation to the thermally cracked radicals is carried out, so that the polycondensation between the thermally cracked radicals is inhibited. As a result, the reactivity is enhanced, so that high oil yield is obtained.

(3) Enhancement of reactivity of hydrocracking due to inhibition of aggregation of micelle structures of asphaltene in heavy oil

The asphaltene component in the heavy oil is considered to form a micelle structure in which several structures each having an average of 5 to 6 aromatic rings as the core, and alkyl groups outside thereof are stacked in several layers.

If the temperature is raised to a reaction temperature of 430 to 455 °C simply (in one step) for heating the raw material slurry up to a reaction temperature of 430 to 455 °C, the stacked

micelle structures aggregate, resulting in a reduction in reactivity of hydrocracking of the heavy oil.

In contrast, upon performing the foregoing pretreating, the oil components in the heavy oil and the oil components formed by thermal cracking of the heavy oil permeate into the micelle structures to inhibit the aggregation of the micelle structures. As a result, the reactivity of hydrocracking of the heavy oil is enhanced. Namely, enough time is given for the oil components to permeate into the micelle structures. Accordingly, the oil components permeate into the micelle structures to inhibit the aggregation of the micelle structures. As a result, the reactivity of hydrocracking of the heavy oil is enhanced.

The reason for setting the temperature condition for the pretreating of the raw material slurry at 320 to 420 °C is as follows. If the temperature condition is less than 320 °C, the reactivity of hydrocracking of a heavy oil is not sufficiently enhanced, and therefore the yield of the upgraded oil is insufficiently enhanced. At not less than 320 °C, the yield of the oil increases with an increase in temperature at temperatures up to the vicinity of 370 °C, and the yield of the oil gradually decreases from a temperature in the vicinity of 370 °C. If the temperature condition is more than 420 °C, the yield of the oil is insufficiently enhanced. Further, the temperature is close to the reaction condition temperature: 430

to 455 °C in the basic reaction step (i.e., there results the same condition as that for the case where the reaction is effected abruptly under the condition of no pretreating). Incidentally, the reason why the yield of the oil gradually decreases from a temperature in the vicinity of 370 °C is considered as follows. If the pretreating temperature increases, the effects of the foregoing items (1) to (3) (enhancement of the catalytic activity due to more smooth proceeding of sulfurization of a limonite ore catalyst; enhancement of the reactivity due to the inhibition of the polycondensation reaction of thermally cracked radicals of a heavy oil; and enhancement of the reactivity of hydrocracking due to the inhibition of aggregation of micelle structures of asphaltene in a heavy oil) are reduced (the resulting operation comes closer to the same operation for no pretreating).

The reason for setting the pretreating time at 10 to 60 minutes is as follows. If the pretreating time is less than 10 minutes, the reactivity of hydrocracking of a heavy oil is not sufficiently enhanced, and therefore the oil yield is insufficiently enhanced. If the pretreating time is not less than 10 minutes and not more than 60 minutes, the longer the time (heating time) is, the more the reactivity of hydrocracking of the heavy oil is enhanced, and the greater the degree of enhancement in yield of the oil is. If the pretreating time is more than 60 minutes, the effect (the effect of enhancement

in yield of the oil due to the enhancement in reactivity of hydrocracking of a heavy oil) almost reaches saturation, resulting in a poor cost efficiency.

It is desirable that the heating temperature for pretreating of the raw material slurry is set at 340 to 400 °C (Second Invention). As a result, it is possible to obtain the effect of enhancement in yield of the oil due to the enhancement in reactivity of hydrocracking of a heavy oil at a higher level. In order for such an effect to be achieved at a still higher level, it is desirable that the heating temperature for pretreating is set at 350 to 390 °C.

If the heating time for pretreating of the raw material slurry is set at not less than 20 minutes, it is possible to obtain the effect of enhancement in yield of the oil due to the enhancement in reactivity of hydrocracking of a heavy oil at a higher level. From the economical point of view, a shorter heating time is better, and the heating time is desirably not more than 40 minutes. It is desirable in terms of these respects that the heating time for the pretreating is set at 20 to 40 minutes (Third Invention). Further, the heating time is desirably 25 to 35 minutes.

For pretreating of the raw material slurry, the heating temperature may be either constant, or changed. Namely, for heating the raw material slurry at a temperature of 320 to 420 °C for 10 to 60 minutes, there may be employed either of the

following methods: a method in which the raw material slurry is held at a temperature (T °C) selected from temperatures of 320 to 420 °C for 10 to 60 minutes (below, also referred to as a constant temperature holding method); and another method in which the raw material slurry is heated from a temperature T_1 to a temperature T_2 in a temperature range (temperature T_1 to temperature T_2) selected from temperatures of 320 to 420 °C over 10 to 60 minutes, i.e., a method in which the time taken to heat the raw material slurry from the temperature T_1 to the temperature T_2 is set to be 10 to 60 minutes (below, also referred to as a temperature changing method). Alternatively, a method of a combination of these methods (below, also referred to as a combination method) may also be employed. This combination method is accomplished, for example, in the following manner. During heating from the temperature T_1 to the temperature T_2 , the temperature is kept at a temperature therebetween for some minutes, so that the total heating time from the temperature T_1 to the temperature T_2 is 10 to 60 minutes. Alternatively, the temperature is held at the temperature T_1 for some minutes, and then raised up to the temperature T_2 , so that the total heating time is 10 to 60 minutes. Incidentally, when the heating temperature for pretreating of the raw material slurry is set at 340 to 400 °C, the foregoing wording "320 to 420 °C" is read instead as "340 to 400 °C". Further, when the heating time for the pretreating is set at 20 to 40 minutes, the foregoing

wording "10 to 60 minutes" is read instead as "20 to 40 minutes".

In the basic reaction step in the method for hydrocracking a petroleum heavy oil in accordance with the present invention, a hydrocracked product of a heavy oil is obtained. It is possible to obtain oils (fractions) having various boiling point ranges from the hydrocracked product by fractionating the product through a process such as distillation. For example, it is possible to obtain gasoline fractions having a boiling point range of that of C₅ to 171 °C, kerosene fractions of 171 to 232 °C, light oil fractions of 232 to 343 °C, heavy oil fractions of 343 to 525 °C, and other fractions. All of these are upgraded oils as compared to the raw material heavy oil.

In the present invention, the petroleum heavy oil containing heavy metals for use as a raw material has no particular restriction. Petroleum heavy oils containing heavy metals such as an atmospheric residue and a vacuum residue are usable. The present invention is also applicable to superheavy oils containing heavy metals such as naturally occurring bitumens (such as tar sands and oil sands). The heavy metals denote the metals which, when a catalyst of Ni-Mo system, Co-Mo system, or the like is used as a catalyst, causes poisoning of the catalyst. The heavy metals have no particular restriction, and examples thereof may include Ni and V.

The amount of a limonite ore as a catalyst to be added in the basic reaction step in the method for hydrocracking a

petroleum heavy oil in accordance with the present invention is desirably 0.3 to 2 mass% in terms of an iron component based on the amount of the petroleum heavy oil. This is due to the following reasons. If the amount of the limonite ore to be added is less than 0.3 mass%, particularly, the yields of an asphaltene component and coke tend to increase. Whereas, if the amount thereof exceeds 2 mass%, the oil yield increasing effect at not more than 450 °C becomes not remarkable. Further, for the amount of sulfur as a promoter to be added, sulfur is desirably added in an amount of not less than one time the iron content of the limonite ore by atomic ratio in order to convert the limonite ore as a catalyst to pyrrhotite exhibiting a catalytic activity. As for the amount above this, for example, sulfur is desirably added in an amount of not more than 3 times the iron content of the limonite ore by atomic ratio from the economical point of view.

As the limonite ore catalyst in the basic reaction step, a powdered limonite ore with a mean particle size of not more than 2 μm is desirably used. This is due to the following reasons. When the mean particle size of the catalyst is large, the contact efficiency between the catalyst and the raw material petroleum heavy oil is low because of the small effective surface area of the catalyst, so that the catalytic activity is low. Whereas, when the mean particle size of the catalyst is as small as not more than 2 μm , the effective surface area

of the catalyst increases, so that the catalytic activity is enhanced. From these respects, a smaller mean particle size of the catalyst is better, and further, the mean particle size is desirably not more than 1 μm .

Such a powdered limonite ore with a mean particle size of not more than 2 μm is obtained by mechanically pulverizing a limonite ore. The pulverization is desirably performed not by a dry process but in a petroleum solvent. This is due to the following reasons. The catalyst obtained from dry pulverization using a jet pulverizer or the like remarkably aggregates in the raw material slurry containing the heavy oil and the catalyst, resulting in an inferior dispersion of the catalyst. In contrast, the catalyst obtained from mechanical pulverization in a petroleum solvent is less likely to aggregate in the foregoing raw material slurry, and excellent in dispersion of the catalyst, resulting in enhanced catalytic activity.

The limonite ore is observed to contain α -iron oxyhydroxide and α -iron oxide as components according to the powder X-ray diffraction analysis. The ratio of the components differs according to the place of production, the mine lot, and the like. Further, a study was made on the effect of the ratio of the components on the catalytic characteristics. As a result, it has been found that a limonite ore which does not substantially contain an iron oxide has the highest catalytic

activity. Therefore, in order to more enhance the catalytic activity, it is desirable to use a limonite ore which does not substantially contain an iron oxide as the limonite ore in the basic reaction step.

There will be explained below the reason why a limonite ore which does not substantially contain an iron oxide has the highest catalytic activity as described above.

An iron-containing compound is generally sulfurized by elemental sulfur or a sulfur compound, so that iron sulfide called pyrrhotite, Fe_{1-x}S , becomes an active species exhibiting a catalytic activity. The lower the temperature at which the conversion to pyrrhotite occurs is, the larger the amount of the active species present before the start of hydrocracking of the raw material targeted for hydrocracking is. Accordingly, sufficient hydrogen atom donation is performed to the thermally cracked radicals occurred from the target raw material. Therefore, polymerization between the thermally cracked radicals is inhibited, so that high oil yield is obtained. Namely, the catalytic activity is high.

α -iron oxyhydroxide has a lower conversion temperature to pyrrhotite than that of α -iron oxide. Therefore, a limonite ore which does not substantially contain iron oxide has the highest catalytic activity. Incidentally, the conversion temperature to pyrrhotite is 200 °C for α -iron oxyhydroxide, and 350 °C for α -iron oxide. It is 350 °C for natural pyrite

(FeS₂) as one example of other iron-based catalysts. These and other facts indicate that α -iron oxyhydroxide is converted to pyrrhotite at a very low temperature. Herein, the term "a limonite ore which does not substantially contain iron oxide" denotes the limonite ore containing α -iron oxide analyzed according to the powder X-ray diffraction analysis in an amount of not more than 10 % by weight (mass).

[Examples]

Below, the present invention will be described by way of examples. However, the present invention is by no way limited to the examples unless departing from its scope.

[Example 1]

A vacuum residue (below, referred to as VR) of a crude oil was used as a petroleum heavy oil containing heavy metals. To the VR, was added a pulverized limonite ore as a catalyst in an amount of 1 mass% in terms of iron based on the amount of the VR. Further, elemental sulfur was added thereto as a promoter in an amount of twice the amount of iron (in an amount of twice the iron content of the limonite ore by atomic ratio), resulting in a raw material slurry. Incidentally, the fraction composition of the VR is as shown in Table 1.

The resulting raw material slurry was charged in a stirred autoclave with an internal volume of 5 liters (below, L). Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set

at 10 MPa (102 kg/cm²). Then, the temperature was raised up to 350 °C in this state, followed by pretreating (pretreating of a constant temperature holding method) in which the raw material slurry was heated at the temperature of 350 °C for 30 minutes. Thereafter, the temperature was raised up to 450 °C to hydrocrack the VR (vacuum residue) under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 4 minutes was taken to raise the temperature from 320 °C to 350 °C, and 17 minutes was taken to raise the temperature from 350 °C to 420 °C. A total of 51 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 30 minutes for pretreating at 350 °C.

After the reaction, the yields of the hydrocracked products such as gases and liquids were determined. The results are shown in Table 2. Incidentally, in Table 2, each yield of the gases and liquids (below, also referred to as fractions and the like) denotes the ratio in wt% (mass%) of each amount of the resulting fractions and the like to the feed of the VR (wt% on feed VR).

As indicated from Tables 1 and 2, the content of fractions with boiling points of not more than 525 °C was 14.64 wt% (mass%) in the raw material VR. However, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of fractions with boiling points of from that of C₅ (C₅H₁₂: pentane)

to 525 °C increased to 74.27 wt%, and the yield of fractions with boiling points of more than 525 °C decreased down to 20.86 wt% by the hydrocracking reaction. Whereas, the coke yield was suppressed at 3.31 wt%.

[Example 2]

The same raw material slurry as that in Example 1 was charged in a stirred autoclave with an internal volume of 5 L. Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set at 10 MPa. Then, the temperature was raised up to 380 °C in this state, followed by pretreating in which the raw material slurry was heated at the temperature of 380 °C for 30 minutes. Thereafter, the temperature was raised up to 450 °C to hydrocrack the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 8 minutes was taken to raise the temperature from 320 °C to 380 °C, and 10 minutes was taken to raise the temperature from 380 °C to 420 °C. A total of 48 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 30 minutes for pretreating at 380 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, roughly the same results as those in Example 1 were obtained. Namely,

the content of fractions with boiling points of not more than 525 °C was 14.64 wt% (mass%) in the raw material VR. However, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of fractions with boiling points of from that of C₅ to 525 °C increased to 76.52 wt%, and the yield of fractions with boiling points of more than 525 °C decreased down to 19.24 wt% by the hydrocracking reaction. Whereas, the coke yield was suppressed at 3.18 wt%.

[Example 3]

The same raw material slurry as that in Example 1 was charged in a stirred autoclave with an internal volume of 5 L. Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set at 10 MPa. Then, the temperature was raised up to 320 °C in this state, followed by pretreating in which the raw material slurry was heated at the temperature of 320 °C for 30 minutes. Thereafter, the temperature was raised up to 450 °C to hydrocrack the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 24 minutes was taken to raise the temperature from 320 °C to 420 °C. A total of 54 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 30 minutes for pretreating at 320 °C.

After the reaction, the yields of respective products

were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the content of fractions with boiling points of not more than 525 °C was 14.64 wt% (mass%) in the raw material VR. However, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of fractions with boiling points of that of C₅ to 525 °C increased to 72.58 wt%, and the yield of fractions with boiling points of more than 525 °C decreased down to 23.21 wt% by the hydrocracking reaction. Whereas, the coke yield was suppressed at 2.85 wt%.

The yield (72.58 wt%) of the fractions with boiling points of that of C₅ to 525 °C after the hydrocracking reaction was lower than the yield (74.27 wt%) for Example 1, but more excellent than the case of Comparative Example 1 described later. The result that Example 3 is thus more excellent in yield of the fractions with boiling points of from that of C₅ to 525 °C than Comparative Example 1 is due to the following fact: the pretreating in which the raw material slurry was heated at 320 °C for 30 minutes was carried out during heating up to the reaction temperature: 450 °C.

[Example 4]

The same raw material slurry as that in Example 1 was charged in a stirred autoclave with an internal volume of 5 L. Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set

at 10 MPa. Then, the temperature was raised up to 420 °C in this state, followed by pretreating in which the raw material slurry was heated at the temperature of 420 °C for 30 minutes. Thereafter, the temperature was raised up to 450 °C to hydrocracking the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 14 minutes was taken to raise the temperature from 320 °C to 420 °C, and a total of 44 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 30 minutes for pretreating at 420 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the content of fractions with boiling points of not more than 525 °C was 14.64 wt% (mass%) in the raw material VR. However, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of the fractions with boiling points of that of from C₅ to 525 °C increased to 70.34 wt%, and the yield of fractions with boiling points of more than 525 °C decreased down to 24.17 wt% by the hydrocracking reaction. Whereas, the coke yield was suppressed at 4.37 wt%.

The yield (70.34 wt%) of the fractions with boiling points of that of C₅ to 525 °C after the hydrocracking reaction was lower than the yield (74.27 wt%) for Example 1, but more

excellent than the case of Comparative Example 1 described later. The result that Example 4 is thus more excellent in yield of the fractions with boiling points of from that of C₅ to 525 °C than Comparative Example 1 is due to the following fact: the pretreating in which the raw material slurry was heated at 420 °C for 30 minutes was carried out during heating up to the reaction temperature: 450 °C.

[Example 5]

The same raw material slurry as that in Example 1 was charged in a stirred autoclave with an internal volume of 5 L. Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set at 10 MPa. Then, the temperature was raised up to 380 °C in this state, followed by pretreating in which the raw material slurry was heated at the temperature of 380 °C for 10 minutes. Thereafter, the temperature was raised up to 450 °C to effect the reaction of hydrocracking the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 8 minutes was taken to raise the temperature from 320 °C to 380 °C, and 10 minutes was taken to raise the temperature from 380 °C to 420 °C. A total of 28 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 10 minutes for pretreating at 380 °C.

After the reaction, the yields of respective products

were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the content of fractions with boiling points of not more than 525 °C was 14.64 wt% (mass%) in the raw material VR. However, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of fractions with boiling points of from that of C₅ to 525 °C increased to 70.53 wt%, and the yield of fractions with boiling points of more than 525 °C decreased down to 24.72 wt% by the hydrocracking reaction. Whereas, the coke yield was suppressed at 4.26 wt%.

The yield (70.53 wt%) of fractions with boiling points of from that of C₅ to 525 °C after the hydrocracking reaction was lower than the yield (74.27 wt%) for Example 1, but more excellent than the case of Comparative Example 1 described later. The result that Example 5 is thus more excellent in yield of the fractions with boiling points of from that of C₅ to 525 °C than Comparative Example 1 is due to the following fact: the pretreating in which the raw material slurry was heated at 380 °C for 10 minutes was carried out during heating up to the reaction temperature: 450 °C.

[Example 6]

The heavy oil components (bottom components, i.e., components with boiling points of not less than 525 °C) obtained in Example 2 was charged together with the raw material VR in an amount of 50 wt% (mass%) based on the amount of the raw

material VR to hydrocrack under the same reaction conditions as those in Example 2. Incidentally, the pulverized limonite ore catalyst was added in an amount of 1 mass% in terms of iron based on the amount of the raw material VR. The elemental sulfur as a promoter was added in an amount of twice the amount of iron as with Example 2.

In this step, the hydrocracking reaction was carried out under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa. However, pretreating in which the raw material slurry was heated at the temperature of 380 °C for 30 minutes was carried out during heating up to the reaction temperature: 450 °C as with Example 2. Thereafter, the temperature was raised up to 450 °C to hydrocrack under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

At this step, 9 minutes was taken to raise the temperature from 320 °C to 380 °C, and 10 minutes was taken to raise the temperature from 380 °C to 420 °C. A total of 49 minutes was taken for the temperature to rise from 320 °C to 420 °C including the 30 minutes for pretreating at 380 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the yield of fractions with boiling points of more than 525 °C was

7.78 wt% (mass%), which was very lower than, and largely reduced from that (19.24 wt%) for Example 2. Whereas, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of the fractions with boiling points of from that of C₅ to 525 °C was 84.58 wt%, which was higher than that (76.52 wt%) for Example 2. The coke yield was suppressed at 3.54 wt%.

Thus, in Example 6, the yield of the fractions with boiling points of more than 525 °C was lower, and the yield of the fractions with boiling points of from that of C₅ to 525 °C was more excellent than in Example 2. This is due to the fact that, in Example 6, the heavy oil components (bottom components) obtained in Example 2 was charged together with the raw material VR, i.e., the so-called bottom recycle was carried out.

The yield (84.58 wt%) of the fractions with boiling points of from that of C₅ to 525 °C in Example 6 was more excellent than that in Comparative Example 3 (with bottom recycle) described later. Whereas, the yield (7.78 wt%) of the fractions with boiling points of more than 525 °C, and the coke yield (3.54 wt%) in Example 6 were lower than those in Comparative Example 1. This is due to the following fact: the pretreating in which the raw material slurry was heated at 380 °C for 30 minutes was carried out during heating up to the reaction temperature: 450 °C.

[Comparative Example 1]

The same raw material slurry as that in Example 1 was

charged in a stirred autoclave with an internal volume of 5 L. Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set at 10 MPa. Then, the temperature was raised up to 450 °C in this state, to hydrocrack the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

Incidentally, the pretreating as in Example 1 was not carried out, and the temperature was raised from room temperature to the reaction temperature: 450 °C in one step, and 8 minutes was taken for the temperature to rise from 320 °C to 420 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of the fractions with boiling points of from that of C₅ to 525 °C was 64.26 wt%, which was lower than that (74.27 wt%) for Example 1. The yield of the fractions with boiling points of more than 525 °C was 28.52 wt%, which was higher than that (20.86 wt%) for Example 1. The coke yield was 5.36 wt%, which was higher than that (3.31 wt%) for Example 1.

[Comparative Example 2]

The same raw material slurry as that in Example 1 was charged in a stirred autoclave with an internal volume of 5 L.

Further, a hydrogen gas was supplied to the autoclave, so that the hydrogen gas supply pressure (reaction pressure) was set at 10 MPa. Then, the temperature was raised up to 310 °C in this state, followed by pretreating in which the raw material slurry was heated at the temperature of 310 °C for 30 minutes. Thereafter the temperature was raised up to 450 °C to hydrocrack the VR under the reaction conditions of reaction temperature: 450 °C, reaction time: 60 minutes, and reaction pressure: 10 MPa.

Incidentally, after the pretreating, the temperature was raised from 310 °C to the reaction temperature: 450 °C in one step. Eight minutes was taken for the temperature to rise from 320 °C to 420 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the yield of fractions with boiling points of not more than 525 °C, i.e., the yield of the fractions with boiling points of from that of C₅ to 525 °C was 66.82 wt%, which was lower than that (72.58 wt%) for Example 3. The yield of the fractions with boiling points of more than 525 °C was 26.91 wt%, which was higher than that (23.21 wt%) for Example 3. The coke yield was 3.29 wt%, which is higher than that (2.85 wt%) for Example 3.

The results indicate as follows. For pretreating the raw material slurry during temperature rising up to reaction

temperature: 450 °C, the pretreating of 30-minute heating at 320 °C produces an effect, while the pretreating of 30-minute heating at 310 °C produces no effect.

[Comparative Example 3]

The bottom recycle was carried out in the same manner as in Example 6 (with the bottom recycle). However, the pretreating as in Example 6 was not carried out, and the temperature was raised from room temperature to the reaction temperature: 450 °C in one step, and 8 minutes was taken for the temperature to rise from 320 °C to 420 °C.

After the reaction, the yields of respective products were determined in the same manner as in Example 1. The results are shown in Table 2. As indicated from Tables 1 and 2, the yield of the fractions with boiling points of not more than 525 °C, i.e., the yield of the fractions with boiling points of from that of C₅ to 525 °C was 74.92 wt%, which was lower than that (84.58 wt%) for Example 6. The yield of the fractions with boiling points of more than 525 °C was 15.49 wt%, which was higher than that (7.78 wt%) for Example 6. The coke yield was 7.29 wt%, which was higher than that (3.54 wt%) for Example 6.

FIG. 1 shows the relationship between the holding temperature (T °C) for the pretreating and the yield of the fractions with boiling points of not more than 525 °C, i.e., the fractions with boiling points of from that of C₅ to 525 °C for the ones subjected to the pretreating of 30-minute heating

at a constant temperature (T °C) (however, except for the ones with bottom recycle) in the foregoing examples (Examples 1 to 6) and comparative examples (Comparative Examples 1 to 3), i.e., for Examples 1 to 4, and Comparative Example 2. FIG. 1 indicates as follows. When the holding temperature is less than 320 °C, the yield of the fractions with boiling points of from that of C_5 to 525 °C (below, oil fractions) is low. Whereas, when the holding temperature is not less than 320 °C, the yield of the oil fractions increases. When the holding temperature is in the vicinity of 370 to 380 °C, the yield of the oil fractions is the highest. When the holding temperature is from the vicinity of 380 °C to 420 °C, the yield of the oil fractions gradually decreases. When the holding temperature exceeds 420 °C, the yield of the oil fractions further decreases, and becomes insufficient.

Incidentally, in the foregoing examples (Examples 1 to 6), and comparative examples (Comparative Examples 1 to 3), the vacuum residue (VR) of a crude oil was used as a petroleum heavy oil containing heavy metals. However, also when the atmospheric residue of a crude oil or an oil sand is used instead, the results of the same tendency as with the foregoing examples and comparative examples can be obtained. In the foregoing examples and comparative examples, the amount of the limonite ore catalyst to be added was set at 1 mass%. However, also when other amounts (ex., 0.5 mass%) is adopted instead, the results

of the same tendency as with the foregoing examples and comparative examples can be obtained. In the foregoing examples and comparative examples, the conditions for the hydrocracking reaction was set as follows: reaction temperature: 450 °C, reaction time: 60 minutes, reaction pressure: 10 MPa. However, also when other conditions are adopted instead (ex.,. both the cases where reaction temperature: 450 °C, reaction time: 90 minutes, reaction pressure: 10 MPa are adopted, and where reaction temperature: 450 °C, reaction time: 60 minutes, reaction pressure: 15 MPa are adopted), the results of the same tendency as with the foregoing examples and comparative examples can be obtained.

[Table 1]

	Fraction composition, wt% on feed VR				
	-232°C	232-343°C	343-450°C	450-525°C	+525°C
Raw material VR	—	—	5.62	9.02	85.36

[Table 2]

	Bottom recycle	Heating – Pretreating temperature / time		Product yield (%VR)			
				C1-C4	C5-525°C	525°C+	Coke
Example-1	None	320→350°C 350°C 350→420°C	4min 30min 17min	4.11	74.27	20.86	3.31
Example-2	None	320→380°C 380°C 380→420°C	8min 30min 17min	3.70	76.52	19.24	3.18
Example-3	None	320°C 320→420°C	30min 24min	3.51	72.58	23.21	2.85
Example-4	None	320→420°C 420°C	14min 30min	4.36	70.34	24.17	4.37
Example-5	None	320→380°C 380°C 380→420°C	8min 10min 10min	3.88	70.53	24.72	4.26
Example-6	Done	320→380°C 380°C 380→420°C	9min 30min 10min	6.95	84.58	7.78	3.54
Comparative Example-1	None	320→420°C	8min	4.50	64.26	28.52	5.36
Comparative Example-2	None	310°C 310→420°C	30min 8min	4.21	66.82	26.91	3.29
Comparative Example-3	Done	320→420°C	8min	8.25	74.92	15.79	7.29

Note) Reaction conditions: the same goes for every case.

(Reaction temperature: 450 °C, Reaction time: 60 minutes, Reaction pressure: 10 MPa)

In accordance with a method for hydrocracking a petroleum heavy oil in accordance with the present invention, it becomes possible to obtain a high distillate (oil) yield economically in hydrocracking a petroleum heavy oil containing heavy metals such as a vacuum residue.

The foregoing invention has been described in terms of preferred embodiments. However, those skilled, in the art will recognize that many variations of such embodiments exist. Such variations are intended to be within the scope of the present invention and the appended claims.

What is claimed is:

1. A method for hydrocracking a petroleum heavy oil containing heavy metals, comprising the steps of:

supplying a raw material slurry containing the heavy oil, a limonite ore and elemental sulfur to a suspended-bed reactor; and

hydrocracking the heavy oil in the reactor under the reaction conditions of reaction pressure: 30 to 160 kg/cm², reaction temperature: 430 to 455°C, and reaction time: 30 to 180 minutes,

wherein said method further comprises a pretreating step in which the raw material slurry is heated at a temperature of 320 to 420°C for 10 to 60 minutes during heating of the raw material slurry up to the reaction temperature.

2. The method for hydrocracking a petroleum heavy oil according to claim 1, wherein the heating temperature in the pretreating is set at 340 to 400°C.

3. The method for hydrocracking a petroleum heavy oil according to claim 1 or 2, wherein the heating time in the pretreating is set at 20 to 40 minutes.

FIG. 1

