A method for hydrocracking petroleum heavy grade oil containing heavy metals in a slurry bed reactor with the help of an iron catalyst is provided. This method includes a step of selectively removing TI (toluene insolubles) by sedimentation solid-liquid separation from the liquid fluid arising from the reaction product. The procedure for separation causes no clogging in the underflow of the settling tank (sedimentation solid-liquid separator) and requires no large settling tank. The selective TI removal is accomplished by using a light solvent for solid-liquid separation which is a mixture composed of aromatic light solvent and self-
supplied light solvent arising from the hydrocracking. The mixed solvent is used in an amount 2 to 5 times the amount of the liquid fluid from which Ti is to be selectively removed, and the sedimentation solid-liquid separator is run at 130-250°C.
ABSTRACT OF THE DISCLOSURE

A method for hydrocracking petroleum heavy grade oil containing heavy metals in a slurry bed reactor with the help of an iron catalyst is provided. This method includes a step of selectively removing TI (toluene insolubles) by sedimentation solid-liquid separation from the liquid fluid arising from the reaction product. The procedure for separation causes no clogging in the underflow of the settling tank (sedimentation solid-liquid separator) and requires no large settling tank. The selective TI removal is accomplished by using a light solvent for solid-liquid separation which is a mixture composed of aromatic light solvent and self-supplied light solvent arising from the hydrocracking. The mixed solvent is used in an amount 2 to 5 times the amount of the liquid fluid from which TI is to be selectively removed, and the sedimentation solid-liquid separator is run at 130-250°C.
METHOD FOR HYDROCRACKING OF PETROLEUM HEAVY OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention:
   The present invention relates to a method for hydrocracking of petroleum heavy grade oil and, more particularly, to a method for hydrocracking of petroleum heavy grade oil containing heavy metals. The method consists of hydrogenating topped crude or vacuum residue in the presence of a catalyst to give highly cracked products.

2. Description of the Related Art:
   The petroleum industry is rapidly changing such that heavy grade oil dominates on the one hand and demands for lighter products increase on the other. This situation has directed people's attention to the cracking technology to produce lighter products in short supply from heavy grade oil in oversupply. The cracking technology is becoming important more and more in the present state of affairs where the petroleum reserve is inevitably decreasing.

   Although there have been proposed many methods for thermal cracking and hydrocracking of heavy grade oil, they still have some problems with cracking of heavy grade oil such as vacuum residue.

   Such heavy grade oil usually contains a large amount of nitrogen compounds and sulfur compounds and hence its cracking in the presence of a catalyst gives rise to products containing extremely harmful organometallic
impurities. These impurities are dominated by nickel (Ni) and vanadium (V). Being chemically combined with comparatively high molecular weight organic compounds such as asphaltene in heavy grade oil, they retard the catalytic activity to decompose and remove nitrogen-, sulfur-, and oxygen-containing compounds.

One method of treating vacuum residue without resorting to catalysts is thermal cracking known as coking process. This method, however, suffers the disadvantage of disposing of a large amount of coke as a by-product. Another disadvantage is low yields due to overcracking that gives more gas than necessary, with recovered oil containing much aromatic and olefinic components detrimental to quality.

The disadvantage of the conventional method is overcome by performing hydrocracking on heavy grade oil which is supplied to a slurry bed reactor together with a cheap disposable iron catalyst and recycled heavy reaction products. This method achieves a high conversion rate exceeding 90% regardless of the type of heavy grade oil under the condition that the reaction pressure is higher than 15 MPa, the temperature is 440-450°C, the reaction time is 60-90 min, and the flow rate of recycled heavy residues (boiling point (b.p.) >525°C) is 10-50 wt% (of the amount of heavy grade oil supplied as the feed stock), on the assumption that the selected iron catalyst is not exceptionally poor in catalytic activity. The

OBJECT AND SUMMARY OF THE INVENTION

Needing high pressure, the hydrocracking method just mentioned above is economically inferior to the thermal cracking method mentioned earlier. Reduction of pressure is essential for this method. In fact, this object is achieved by employing a cheap active iron catalyst such as natural limonite (iron ore). This catalyst allows for hydrocracking at 10 MPa to attain a conversion rate exceeding 90% under the above-mentioned condition (reaction temperature, reaction time, and flow rate of recycled residues). Nevertheless, the hydrocracking at a low pressure still has the disadvantage of yielding a large amount of coke when applied to heavy grade oil containing asphaltene with more than 13 condensed rings. (This coke is insoluble in toluene and hence it will be referred to as toluene insolubles or TI hereinafter.) This causes an increase of Ti concentration in the bottom or heavy residues (b.p. >525°C) after repeated recycling and the heavy residues (bottom) eventually become hard to decompose because TI is very little reactive to decomposition. The result is ineffective bottom recycling and low conversion rates and yields.

An effective way of suppressing TI is to raise the reaction pressure. However, this is economically
unfavorable. In order to keep low the concentration of TI in the recycled heavy residues even though the amount of TI increases under the low-pressure condition, it is necessary to selectively remove TI from the system.

Selective removal of TI from the system is accomplished by the method of sedimentation solid-liquid separation with solvent addition, which consists of adding light solvent to heavy reaction products (containing heavy residues and solids) in a settling tank and discharging soluble matter from the overflow and insoluble matter (mostly TI and catalyst) from the underflow. Unfortunately, this method cannot use a light product arising from hydrocracking as the light solvent because of low solubility for heavy organic matter. The result of low solubility is coagulation and clogging with solids in the underflow. This problem does not exist with an aromatic light solvent (such as toluene) capable of readily solubilizing heavy organic matter.

However, an aromatic light solvent poses another problem with very slow sedimentation of solids, and addressing this problem needs a huge settling tank with a large equipment cost. Moreover, an aromatic light solvent is several times higher in production cost than a naphtha fraction having approximately the same boiling point. When used alone for solid-liquid separation, its loss results in greatly increasing of the process cost.

The foregoing has aroused a demand for an inexpensive
method for selective TI removal (solid-liquid separation) that permits the economical treating of heavy grade oil with a high TI yield.

The present invention was completed in view of the foregoing. It is an object of the present invention to provide a method for hydrocracking of heavy grade oil which permits selective removal of TI by sedimentation solid-liquid separation in slurry bed hydrocracking with an iron catalyst, without causing clogging in the underflow of the settling tank and requiring a large settling tank.

The present invention relates to a method for hydrocracking of petroleum heavy grade oil as defined below.

The first aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil which comprises steps of supplying a slurry bed reactor with a petroleum heavy grade oil containing heavy metal components together with an iron catalyst to perform hydrocracking on the petroleum heavy grade oil, transferring the reaction products from the slurry bed reactor to a gas-liquid separator to separate the gas fluid from the liquid fluid (containing solids), recycling part of the liquid fluid to the slurry bed reactor and mixing the remainder with a light solvent for solid-liquid separation and performing solid-liquid separation on the resulting mixture in a sedimentation solid-liquid separator, and recovering the light solvent for solid-liquid separation from the fluid extracted from the overflow in the solid-liquid.
separator and subsequently recycling the fluid partly or entirely to the slurry bed reactor, wherein the solvent for solid-liquid separation is a mixture of an aromatic light solvent and a light solvent arising from the hydrocracking and this mixed solvent is added in amount two to five times the amount of the remainder of the liquid fluid, with the sedimentation solid-liquid separator kept at 130-250°C.

The second aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in the first aspect, wherein the aromatic light solvent is composed of a single component with a boiling point lower than 150°C or a mixture of such components.

The third aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in the first or second aspect, wherein the light solvent arising from the hydrocracking, which is mixed with the aromatic light solvent, has a boiling point in the range of 80 to 180°C.

The fourth aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in any of the first to third aspects, wherein the mixing ratio of the aromatic light solvent and the light solvent arising from the hydrocracking is from 30/70 to 60/40.

The fifth aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in any of the first to fourth aspects, wherein
reaction in the slurry bed reactor is carried out under the condition that the reaction pressure is 6 to 14 MPaG, the reaction temperature is 430 to 450°C, and the reaction time is 30 to 120 min.

The sixth aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in any of the first to fifth aspects, wherein the iron catalyst is a powdery limonite iron ore in the form of fine particles with an average particle diameter smaller than 2 μm which has been prepared by mechanical pulverizing in a petroleum solvent and it is added in an amount of 0.3 to 2 wt% (in terms of iron) of the amount of the petroleum heavy grade oil.

The seventh aspect of the present invention is directed to a method for hydrocracking of petroleum heavy grade oil as defined in any of the first to sixth aspects, wherein the fluid which has been extracted from the overflow in the solid-liquid separator and which remains after removal of the light solvent for solid-liquid separation is recycled to the slurry bed reactor in such an amount that its fraction having a boiling point higher than 525°C accounts for 10 to 100 wt% of the amount of the petroleum heavy grade oil being supplied to the slurry bed reactor.

[Effect of the invention]

The method according to the present invention allows for hydrocracking of petroleum heavy grade oil with the
help of an iron catalyst in a slurry bed reactor, which involves selective TI removal by sedimentation solid-liquid separation, without causing clogging with the underflow in the settling tank and requiring a large settling tank.

**BRIEF DESCRIPTION OF THE DRAWING**

Fig. 1 is a flow diagram illustrating the method for hydrocracking of petroleum heavy grade oil according to the present invention.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

After their extensive investigation to achieve the above-mentioned object, the present inventors devised an improved method for selective TI removal by sedimentation solid-liquid separation in hydrocracking by the slurry bed system that employs an iron catalyst. The improved method is characterized in that the liquid fluid containing solids is given for solid-liquid separation of a mixture of aromatic light solvent and self-supplied light solvent arising from hydrocracking and that the amount of the mixture is 2 to 5 times the amount of the liquid fluid and the sedimentation solid-liquid separation is carried out at 130 to 250°C. It permits selective TI removal while allowing the underflow in the settling tank (sedimentation solid-liquid separator) to flow smoothly without clogging and also requiring no large settling tank.

The foregoing improved method for hydrocracking of petroleum heavy grade oil is defined by the first aspect of the present invention as follows. It comprises steps of
supplying a slurry bed reactor with a petroleum heavy grade oil containing heavy metal components together with an iron catalyst to perform hydrocracking on the petroleum heavy grade oil, transferring the reaction products from the slurry bed reactor to a gas-liquid separator to separate the gas fluid from the liquid fluid (containing solids), recycling part of the liquid fluid to the slurry bed reactor and mixing the remainder with a light solvent for solid-liquid separation and performing solid-liquid separation on the resulting mixture in a sedimentation solid-liquid separator, and recovering the light solvent for solid-liquid separation from the fluid extracted from the overflow in the solid-liquid separator and subsequently recycling the fluid partly or entirely to the slurry bed reactor, wherein the solvent for solid-liquid separation is a mixture of an aromatic light solvent and a light solvent arising from the hydrocracking and this mixed solvent is added in an amount two to five times the amount of the remainder of the liquid fluid, with the sedimentation solid-liquid separator kept at 130-250°C.

Incidentally, the step of gas-liquid separation (to separate the reaction product from the slurry bed reactor into a gas fluid and a liquid fluid containing solids) should preferably be carried out in three stages at high pressure, low pressure, and vacuum pressure.

According to the first aspect of the present invention, the method for hydrocracking of petroleum heavy grade oil
offers the advantage of removing TI selectively without causing clogging with the underflow in the settling tank (sedimentation solid-liquid separator) and requiring any large settling tank.

According to the first aspect of the present invention, the method for hydrocracking of petroleum heavy grade oil is characterized in that the solvent for solid-liquid separation is added in an amount two to five times the amount of the liquid fluid (or part of the liquid fluid separated by the reduced pressure gas-liquid separator) from which solids are to be separated. The reason for this is that the amount less than the lower limit does not let solid components (coke and catalyst) settle at a desirable rate and the amount more than the upper limit makes the process uneconomical because of the necessity of refinishing solvent lost from the solvent recycling system.

According to the first aspect of the present invention, the method for hydrocracking of petroleum heavy grade oil is characterized in that the sedimentation solid-liquid separator is operated at 130-250°C. The reason for this is that operation at temperatures below 130°C does not let solid components (coke and catalyst) settle at a desirable rate and operation at temperatures above 250°C needs expensive facilities which withstands a pressure exceeding 2 MPa in order to keep the solvent (having a high vapor pressure) in a liquid state.

According to the first aspect of the present invention,
the method for hydrocracking of petroleum heavy grade oil is characterized in that the light solvent used for solid-liquid separation is a mixture of aromatic light solvent and self-supplied light solvent arising from hydrocracking. According to the second aspect of the present invention, the aromatic light solvent should be one having a boiling point lower than 150°C in pure or mixed form. It includes, for example, benzene and toluene.

According to the third aspect of the present invention, the self-supplied light solvent (arising from hydrocracking) to be mixed with the aromatic light solvent should be one having a boiling point of 80-180°C. The reason for this is that the one having a boiling point lower than 80°C raises the vapor pressure of the mixed solvent (for solid-liquid separation), which necessitates expensive facilities, and the one having a boiling point higher than 180°C uneconomically needs a large amount of heat for solvent recovery from the fluid discharged from the overflow and underflow in the solid-liquid separator.

According to the fourth aspect of the present invention, the light solvent for solid-liquid separation should be composed of an aromatic light solvent and a self-supplied light solvent in a ratio of from 30/70 to 60/40. The reason for this is that the mixed solvent for solid liquid separation in which the self-supplied light solvent accounts for more than 70 wt% or the mixing ratio is smaller than 30/70 is liable to cause clogging with solids
in the bottom of the sedimentation solid-liquid separator, disabling normal operation, and that the mixed solvent for solid liquid separation in which the self-supplied light solvent accounts for less than 40 wt% or the mixing ratio is larger than 60/40 is liable to retard solids from settling in the sedimentation solid-liquid separator, resulting in uneconomical operation with an enlarged sedimentation solid-liquid separator and a larger amount of aromatic light solvent added thereto.

According to the fifth aspect of the present invention, the reaction in the slurry bed reactor should be carried out under the condition that the reaction pressure is 6 to 14 MPaG, the reaction temperature is 430 to 450°C, and the reaction time is 30 to 120 min. Incidentally, the reaction pressure is expressed in terms of gauge pressure. 1 MPaG is equal to 1.1 MPa in terms of absolute pressure. Normal pressure is 0 MPa in terms of gauge pressure and 0.101 MPa in terms of absolute pressure. 1 MPaG = 1 x 10^6 Pa and 9.080665 x 10^4 Pa = 1 kgf/cm² (or 0.980665 x 10^5 Pa = 1 kgf/cm²), and hence 0.980665 MPa = 10 kgf/cm². This means that the pressure of 6 to 14 MPaG is equivalent to 6 x 10/0.980665 to 14 x 10/0.980665 kgf/cm².

According to the sixth aspect of the present invention, the method for hydrocracking of heavy grade oil employs as an iron catalyst a powdery limonite iron ore in the form of fine particles with an average particle diameter smaller than 2 μm which has been prepared by mechanical pulverizing.
in a petroleum solvent and it is added in an amount of 0.3 to 2 wt% (in terms of iron) of the amount of the petroleum heavy grade oil. Limonite iron ore as a catalyst is more active than hematite (Fe₂O₃), pyrite (FeS₂), and iron sulfate (FeSO₄), and is a cheap naturally occurring catalyst. With an amount less than 0.3 wt%, it causes coke to occur in large amounts. With an amount more than 2 wt%, it makes production cost high without increasing oil yields.

According to the seventh aspect of the present invention, the method for hydrocracking of petroleum heavy grade oil includes the steps of separating the light solvent for solid liquid separation from the fluid discharged from the overflow in the solid-liquid separator and recycling the separated fluid partly or entirely to the slurry bed reactor. The amount of the fluid to be recycled to the slurry bed reactor should be such that the amount of heavy residues (bottom) with a boiling point higher than 525°C in the fluid is 10 to 100 wt% of the amount of the petroleum heavy grade oil supplied.

The reason for this is that recycling with an amount less than 10 wt% does not increase oil yields and is poor in the effect of bottom recycling and that recycling with an amount more than 100 wt% does not increase oil yield so much as recycling with an amount specified above although it increases oil yields more than recycling with an amount less than 10 wt%.

According to the present invention, the light solvent
used for solid-liquid separation is a mixture of aromatic light solvent and self-supplied light solvent arising from the hydrocracking process. In the initial stage of operation, the self-supplied light solvent is light oil, such as naphtha, obtained by distillation of the gas fluid and/or the liquid fluid which has been separated in the gas separator placed downstream the reactor. (This solvent will be referred to as “light oil A obtained by distillation” hereinafter.) It is mixed with aromatic light solvent and the resulting mixture is used as the light solvent for solid liquid separation. In the subsequent stages, the light solvent for solid liquid separation is obtained by separation from the fluid discharged from the overflow in the solid-liquid separator. (The resulting solvent is referred to as “solvent a” hereinafter.) The light solvent for solid liquid separation is also obtained by separation from the fluid discharged from the underflow in the solid-liquid separator. (The resulting solvent is referred to as “solvent b” hereinafter.) The light solvent for solid-liquid separation is also prepared by separating the light solvent for solid-liquid separation from the fluid discharged from the overflow and/or the underflow in the solid-liquid separator and then distilling the separated light solvent to give light oil, such as naphtha, (which is referred to as “light oil B obtained by distillation” hereinafter) and mixing it with purchased aromatic light oil. (The
resulting solvent is referred to as "solvent c" hereinafter.) Two or more of solvent a, solvent b, and solvent c mentioned above are used as the light solvent for solid-liquid separation. When in short, the thus prepared light solvent for solid-liquid separation is supplemented with light oil A obtained by distillation and aromatic light solvent individually or in combination.

According to the present invention, the light solvent used for solid-liquid separation is a mixture of aromatic light solvent and self-supplied light solvent arising from the hydrocracking process. The latter includes light oil A and light oil B as well as light solvents (excluding aromatic light solvent) selected from solvent a, solvent b, and solvent c mentioned above.

According to the present invention, the method for hydrocracking of petroleum heavy grade oil includes the step of supplying the reaction product from the slurry bed reactor to the high-pressure gas-liquid separator for separation into gas fluid and liquid fluid (containing solids). The liquid fluid contains heavy oil components and solids (coke and catalyst) as well as light oil components. The heavy oil components are those having a boiling point higher than 525°C and the light oil components are those having a boiling point lower than that of the heavy oil components.

The liquid fluid is subsequently supplied to the low-pressure gas-liquid separator for separation into gas fluid
and liquid fluid (containing solids). The liquid fluid is supplied to the vacuum gas-liquid separator for separation into gas fluid and liquid fluid (containing solids). The liquid fluid contains heavy oil components and solids as well as light oil components. Incidentally, the liquid fluid is composed of light oil components and heavy oil components dissolved therein and it also contains solids.

The liquid fluid is partly recycled to the slurry bed reactor and the remainder of the liquid fluid is mixed with the light solvent for solid-liquid separation and the resulting mixture is supplied to the sedimentation solid-liquid separator for sedimentation of solids. The fluid containing a less amount of solids is discharged from the upper part of the solid-liquid separator and the fluid containing a larger amount of solids is discharged from the lower part of the solid-liquid separator. The fluid discharged from the upper part of the solid-liquid separator contains heavy oil components, light oil components, and light solvent for solid-liquid separation. It is composed of light oil components and light solvent for solid-liquid separation and heavy oil components dissolved in the former two. On the other hand, the fluid discharged from the lower part of the solid-liquid separator contains solids (coke and catalyst) insoluble in light solvent for solid-liquid separation as well as oil components. It is a slurry composed of oil components and solid components.
According to the present invention, the method for hydrocracking of petroleum heavy grade oil is accomplished by using the apparatus shown in Fig. 1, which is comprised of (1) slurry preparation vessel, (2) preheater, (3) slurry bed reactor, (4) high pressure gas-liquid separator, (5) low-pressure gas-liquid separator, (6) vacuum gas-liquid separator, (7) slurry preparation vessel, (8) sedimentation solid-liquid separator (settling tank), (9) apparatus to recover solvent from overflow, (10) apparatus to recover solvent from underflow, (11) high-pressure low-temperature gas-liquid separator, (12) gas purification unit, and (13) distillation column. The foregoing apparatus is operated as follows for the hydrocracking of petroleum heavy grade oil according to the present invention.

The slurry preparation vessel (1) is supplied with petroleum heavy grade oil (containing heavy metals) together with iron catalyst. After mixing, the resulting mixture (slurry) is fed to the preheater (2), which is also supplied with hydrogen. The preheated mixture (including hydrogen) is fed to the slurry bed reactor (3), in which hydrocracking of petroleum heavy grade oil takes place.

The reaction product from the slurry bed reactor (3) is fed to the high-pressure gas-liquid separator (4), in which separation of gas fluid and liquid fluid (containing solids) takes place. The separated liquid fluid is fed to the low-pressure gas-liquid separator (5), in which separation of gas fluid and liquid fluid (containing...
solids) takes place. The liquid fluid is fed to the vacuum gas-liquid separator (6), in which separation of gas fluid and liquid fluid (containing solids) takes place. The liquid fluid is partly recycled to the slurry bed reactor (3) mentioned above, and the remainder of the liquid fluid is fed, together with the light solvent for solid-liquid separation, to the slurry preparation vessel (7) for their mixing.

Here, the light solvent used for solid-liquid separation is a mixture of aromatic light solvent and self-supplied light solvent arising from hydrocracking, and it is mixed with the remainder of the liquid fluid supplied to the slurry preparation vessel (7), with the mixing ratio being two to five times. Incidentally, the self-supplied light solvent is naphtha arising from the distillation column (13). In the early stage of operation, a mixture of this naphtha and aromatic light solvent is used as the solvent for solid liquid separation. After that, it is switched to "solvent a" separated from the apparatus (9) to recover solvent from the overflow or "solvent b" separated from the apparatus (10) to recover solvent from the underflow (as mentioned later). When the amount is short, these solvents for solid-liquid separation are supplemented with aromatic light solvent and naphtha arising from the distillation column (13).

The mixture (slurry) arising from the slurry preparation vessel (7) is fed to the sedimentation solid-
liquid separator (8) which allows solids to settle, with the fluid containing less solids being discharged from its upper part and the fluid containing more solids being discharged from its lower part. Incidentally, the sedimentation solid-liquid separator (8) is run at 130 to 250°C.

The fluid discharged from the upper part of the solid-liquid separator (8) is fed to the overflow solvent recovery apparatus (9) from which the light solvent for solid-liquid separation is removed. The removed fluid is partly recycled to the slurry bed reactor (3) through the slurry preparation vessel (1) and the preheater (2), with the remainder being fed to the distillation column (13). The light solvent for solid-liquid separation recovered in the solvent recovery apparatus (9) is fed to the slurry preparation vessel (7) in which it is used for solid-liquid separation.

The fluid discharged from the lower part of the solid-liquid separator (8) is fed to the underflow solvent recovery apparatus (10) from which the light solvent for solid-liquid separation is removed, with the residues (sludge) being discharged from the system.

Incidentally, the gas fluid separated by the high-pressure gas-liquid separator (4) is fed to the high-pressure low-temperature gas-liquid separator (11) and the gas separated in the separator (11) is supplied to the gas purification unit (12). The gas fluid separated by the
low-pressure gas-liquid separator (5) and the vacuum gas-liquid separator (6) is fed, together with liquid fluid separated by the high-pressure low-temperature gas-liquid separator (11), to the distillation column (13).

EXAMPLES

The invention will be described in more detail with reference to the following Example and Comparative Examples, which are not intended to restrict the scope thereof and which may be modified in any manner within the scope thereof.

Example 1

Hydrocracking was performed on petroleum heavy grade oil containing heavy metals by using an apparatus equivalent to that shown in Fig. 1. A detailed description follows.

The slurry preparation vessel (1) is charged with petroleum heavy grade oil containing heavy metals, an iron catalyst, and a co-catalyst. After mixing, the resulting mixture (slurry) is supplied to the preheater (2), which is also fed with hydrogen. After preheating, the resulting mixture is fed, together with hydrogen, to the slurry bed reactor (3). Incidentally, the petroleum heavy grade oil containing heavy metals is vacuum residues (VR for short hereinafter). The iron catalyst is limonite iron ore, which is used in an amount of 1 wt% (in terms of iron) for the amount of the petroleum heavy grade oil. The co-catalyst is sulfur, which is used in an amount of 1.2 times the amount
of the iron component. Hydrocracking in the slurry bed reactor (3) is carried out under the following conditions. Reaction pressure: 12 MPa, reaction temperature: 450°C, reaction time: 90 min, and amount of heavy residues (b.p. >525°C) recycled: 50 wt%. The fractions of VR are shown in Table 1 (in which "wt% on feed VR" means the ratio (in wt%) of VR (by weight) fed.

Table 1

<table>
<thead>
<tr>
<th>Composition of distillate (wt% on feed VR)</th>
<th>&lt;171°C</th>
<th>171-232°C</th>
<th>232-343°C</th>
<th>343-525°C</th>
<th>&gt;525°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed VR</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>16.4</td>
<td>83.6</td>
</tr>
</tbody>
</table>

The slurry bed reactor (3) supplies its reaction product to the high-pressure gas-liquid separator (4) for separation into gas fluid and liquid fluid (containing solids). The liquid fluid enters the low-pressure gas-liquid separator (5) for separation into gas fluid and liquid fluid (containing solids). The liquid fluid enters the vacuum gas-liquid separator (6) for separation into gas fluid and liquid fluid (containing solids). The high-pressure gas-liquid separator (4) runs at 12 MPaG and 400°C, the low-pressure gas-liquid separator (5) runs at 0.3 MPaG and 380°C, and the vacuum gas-liquid separator runs at 10 mmHg and 350°C. The liquid fluid separated by the vacuum gas-liquid separator (6) has the composition as shown in Table 2. In Table 2, BTM (>525°C) denotes a mixture of heavy organic matter having a boiling point higher than 525°C and inorganic matter (catalyst), HS components denote
those which are soluble in hexane, and HI-TS components denote those which are insoluble in hexane and soluble in toluene. These terms are also used in Tables 3 and 4 later.

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition of liquid fluid from vacuum gas-liquid separator to settling tank (wt%)</th>
<th>Composition of liquid fluid from upper part of settling tank (wt%)</th>
<th>Composition of liquid fluid from lower part of settling tank (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (b.p. 343-525°C)</td>
<td>45.81</td>
<td>53.18</td>
<td>29.47</td>
</tr>
<tr>
<td>BTM (&gt;525°C)</td>
<td>(54.19)</td>
<td>(46.81)</td>
<td>(70.54)</td>
</tr>
<tr>
<td>HS components</td>
<td>24.96</td>
<td>28.97</td>
<td>16.06</td>
</tr>
<tr>
<td>HI-TS components</td>
<td>14.65</td>
<td>15.64</td>
<td>12.45</td>
</tr>
<tr>
<td>TI components</td>
<td>9.77</td>
<td>2.13</td>
<td>26.71</td>
</tr>
<tr>
<td>Catalyst</td>
<td>4.81</td>
<td>0.07</td>
<td>15.32</td>
</tr>
</tbody>
</table>

The liquid fluid separated by the vacuum gas-liquid separator (6) enters, together with the light solvent for solid-liquid separation, the slurry preparation vessel (7) for their mixing. The light solvent for solid-liquid separation is a mixture of aromatic light solvent and self-supplied light solvent arising from the hydrocracking process. Its amount is four times the amount of the liquid fluid supplied to the slurry preparation vessel (7). The aromatic light solvent is toluene, and the self-supplied light solvent is naphtha (b.p.: 100-170°C) arising from the distillation column (13). They are mixed in a ratio of 40/60.

This mixture prepared in the slurry preparation vessel (7) enters the sedimentation solid-liquid separator (8) in which solids settle. The sedimentation solid-liquid
separator (8) discharges a fluid with less solids from its upper part and discharges a fluid with more solids from its lower part. It runs at 1.5 MPa and 220°C.

The fluid from the upper part of the solid-liquid separator (8) has the light solvent for solid-liquid separation separated. The fluid, after the separation of the light solvent separated, has the composition as shown in Table 2. The fluid from the lower part of the solid-liquid separator (8) has the light solvent for solid-liquid separation separated. The fluid, after the separation of the light solvent, has the composition as shown in Table 2. It is noted from Table 2 that the liquid fluid from the lower part of the solid-liquid separator (8) contains concentrated TI (toluene insolubles) and catalyst and that the liquid fluid from the upper part of the solid-liquid separator (8) contains less TI and catalyst.

Part of the fluid from the upper part of the solid-liquid separator (8), after the separation of the light solvent, is recycled to the reaction system together with the liquid fluid from the vacuum gas-liquid separator (6).

The above-mentioned hydrocracking of petroleum heavy grade oil successfully achieves the selective TI removal by sedimentation solid-liquid separation without clogging in the underflow of the settling tank (sedimentation solid-liquid separator) (8) and without the necessity of enlarging the settling tank.

The slurry bed reactor achieves reactions effectively
such that the rate of conversion is 91%, the yield of heavy residues (b.p. >525°C) is 7.5 wt% of the amount of feed VR, and the yield of oil is 85 wt% of the amount of feed VR. Here, the rate of conversion is calculated from the following formula (1).

\[
\text{Rate of conversion (\%)} = \frac{(A - B)}{A} \times 100 \quad \cdots (1)
\]

(where A is the amount (wt%) of heavy residues (b.p. >525°C) in feed VR and B is the yield of heavy residues.)

**Comparative Example 1**

The same procedure as in Example 1 was repeated for hydrocracking of petroleum heavy grade oil except that the light solvent for solid liquid separation is composed solely of self-supplied light solvent, which is naphtha (b.p.: 100-170°C) arising from the distillation column (13).

The result was that clogging occurred in the lower part of the settling tank (sedimentation solid-liquid separator) (8), which discontinued operation. The solid substance that caused clogging was found to have the composition shown in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition of solid substance remaining in lower part of settling tank (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS components</td>
<td>5.4</td>
</tr>
<tr>
<td>HI-TS components</td>
<td>19.3</td>
</tr>
<tr>
<td>TI components</td>
<td>46.2</td>
</tr>
<tr>
<td>Catalyst</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Comparative Example 2

The same procedure as in Example 1 was repeated for hydrocracking of petroleum heavy grade oil except that the light solvent for solid liquid separation is composed solely of aromatic light solvent, which is toluene (b.p.: 110°C).

The result was that the solid-liquid separator (8) allowed fluids to be discharged from its upper and lower parts without clogging. The composition of the fluids, after the separation of the light solvent for solid-liquid separation is shown in Table 4.

Table 4

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition of liquid fluid from upper part of settling tank (wt%)</th>
<th>Composition of liquid fluid from lower part of settling tank (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (b.p. 343-525°C)</td>
<td>50.22</td>
<td>33.89</td>
</tr>
<tr>
<td>BTM (&gt;525°C)</td>
<td>(49.78)</td>
<td>(66.12)</td>
</tr>
<tr>
<td>HS components</td>
<td>27.36</td>
<td>18.46</td>
</tr>
<tr>
<td>HI-TS components</td>
<td>15.58</td>
<td>12.14</td>
</tr>
<tr>
<td>TI components</td>
<td>6.70</td>
<td>18.09</td>
</tr>
<tr>
<td>Catalyst</td>
<td>0.14</td>
<td>17.43</td>
</tr>
</tbody>
</table>

Despite continued operation without clogging in the lower part of the settling tank (sedimentation solid-liquid separator) (8), the procedure in Comparative Example 2 is less satisfactory in selective TI removal than that in Example 1 as indicated by Table 4. That is, the fluid from the lower part of the solid-liquid separator (8) contains TI components and catalyst remaining with a low degree of
concentration and the fluid from the upper part of the solid-liquid separator (8) contains TI components and catalyst in large amounts (indicating a low ratio of TI removal and insufficient selective TI removal).

The fluid discharged from the upper part of the solid-liquid separator (8) enters the solvent recovery apparatus (9) in which the light solvent for solid-liquid separation is separated. Part of the fluid discharged from the apparatus (9) is recycled to the reaction system together with the liquid fluid separated by the vacuum gas-liquid separator (6). The slurry bed reactor achieved reactions such that the conversion rate is 87%, the yield of heavy residues (b.p. >525°C) is 11.4 wt% on feed VR, and the yield of oil is 82 wt% on feed VR.

It is noted from the foregoing that the procedure in Example 1 and Comparative Example 2 permits selective TI removal without clogging in the lower part of the settling tank unlike the procedure in Comparative Example 1. The procedure in Comparative Example 2, however, is poor in the ratio of TI removal and insufficient in selective TI removal. In addition, it is uneconomical because it relies on only aromatic light solvent as the solvent for solid-liquid separation. The procedure in Example 1 is superior to that in Comparative Example 2 in that it performs selective TI removal effectively and it is economical because it employs a mixture of aromatic light solvent and self-supplied light solvent as the solvent for solid-liquid separation.
The present invention provides a method for hydrocracking petroleum heavy grade oil containing heavy metals in a slurry bed reactor with the help of an iron catalyst. This method includes a step of selectively removing Ti by sedimentation solid-liquid separation from the liquid fluid arising from the reaction product. The procedure for separation causes no clogging in the underflow of the settling tank (sedimentation solid-liquid separator) and requires no large settling tank. Therefore, the method of the present invention is suitable for hydrocracking of heavy grade oil containing heavy metals.
WHAT IS CLAIMED IS:

1. A method for hydrocracking of petroleum heavy grade oil which comprises steps of:

   supplying a slurry bed reactor with a petroleum heavy grade oil containing heavy metal components together with an iron catalyst to perform hydrocracking on the petroleum heavy grade oil;

   transferring the reaction products from the slurry bed reactor to a gas-liquid separator to separate the gas fluid from the liquid fluid (containing solids);

   recycling part of the liquid fluid to the slurry bed reactor and mixing the remainder with a light solvent for solid-liquid separation and performing solid-liquid separation on the resulting mixture in a sedimentation solid-liquid separator; and

   recovering the light solvent for solid-liquid separation from the fluid extracted from the overflow in the solid-liquid separator and subsequently recycling the fluid partly or entirely to the slurry bed reactor,

   wherein the solvent for solid-liquid separation is a mixture of an aromatic light solvent and a light solvent arising from the hydrocracking and this mixed solvent is added in amount two to five times the amount of the remainder of the liquid fluid, with the sedimentation solid-liquid separator kept at 130-250°C.

2. The method for hydrocracking of petroleum heavy grade oil as defined in Claim 1, wherein the aromatic light
solvent is composed of a single component with a boiling point lower than 150°C or a mixture of such components.

3. The method for hydrocracking of petroleum heavy grade oil as defined in Claim 1 or 2, wherein the light solvent arising from the hydrocracking, which is mixed with the aromatic light solvent, has a boiling point in the range of 80 to 180°C.

4. The method for hydrocracking of petroleum heavy grade oil as defined in any of Claims 1 to 3, wherein the mixing ratio of the aromatic light solvent and the light solvent arising from the hydrocracking is from 30/70 to 60/40.

5. The method for hydrocracking of petroleum heavy grade oil as defined in any of Claims 1 to 4, wherein reaction in the slurry bed reactor is carried out under the condition that the reaction pressure is 6 to 14 MPaG, the reaction temperature is 430 to 450°C, and the reaction time is 30 to 120 min.

6. The method for hydrocracking of petroleum heavy grade oil as defined in any of Claims 1 to 5, wherein the iron catalyst is a powdery limonite iron ore in the form of fine particles with an average particle diameter smaller than 2 μm which has been prepared by mechanical pulverizing in a petroleum solvent and it is added in an amount of 0.3 to 2 wt% (in terms of iron) of the amount of the petroleum heavy grade oil.

7. The method for hydrocracking of petroleum heavy
grade oil as defined in any of Claims 1 to 6, wherein the fluid which has been extracted from the overflow in the solid-liquid separator and which remains after removal of the light solvent for solid-liquid separation is recycled to the slurry bed reactor in such an amount that its fraction having a boiling point higher than 525°C accounts for 10 to 100 wt% of the amount of the petroleum heavy grade oil being supplied to the slurry bed reactor.