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PROCESS FOR HYDROTREATING HEAVY HYDROCARBON OIL

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(57) Claim

1. A process for hydrogenating a heavy hydrocarbon oil including the successive steps of

(a) hydrogenating-demetalizing a heavy hydrocarbon oil in the presence of hydrogen and a hydrogenating-demetalizing catalyst, to produce a hydrogenated, demetalized oil,

(b) hydrocracking the hydrogenated, demetalized oil from step (a) in the presence of hydrogen and a hydrocracking catalyst to produce a hydrocracked oil, and

(c) hydrodesulfurizing-hydrodenitrifying said hydrocracked oil from step (b) in the presence of hydrogen and a hydrodesulfurizing-hydrodenitrifying catalyst, said hydrodesulfurizing-hydrodenitrifying catalyst having a pore size distribution as measured by a nitrogen release method in which an average pore diameter of the pores having a diameter of 16 to 1700 Å is from 55 to 90 Å, the volume of the pores having said average pore diameter ±10 Å occupies at least 30% of the volume occupied by the pores having a diameter of 16 to 1,700 Å and the volume of the pores having a diameter of not smaller than 101 Å occupies at most 10% of the volume occupied by the pores having a diameter of 16 to 1,700 Å.

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(54) Title : PROCESS FOR HYDROTREATING HEAVY HYDROCARBON OIL

(54) 発明の名称 重質炭化水素油の水素化処理方法

(57) Abstract

A process for catalytically hydrotreating heavy hydrocarbon oil which comprises sequentially conducting (1) hydrodemetallization, (2) hydrocracking and (3) hydro-desulfurization and denitrification, and uses a catalyst having a pore size distribution restricted to a specified range when determined by the nitrogen desorption method in the hydro-desulfurization and denitrification step. This process can provide an oily product having a reduced sulfur content at a high cracking ratio and is free from the troubles of the apparatus caused by sludge.

DESCRIPTION

PROCESS FOR HYDROGENATING TREATMENT OF HEAVY HYDROCARBON OIL

TECHNICAL FIELD

The present invention relates to a process for hydrogenating treatment of a heavy hydrocarbon oil. More particularly, it pertains to a process for hydrogenating treatment of a heavy hydrocarbon oil which process is capable of efficiently producing a product oil with a low sulfur content in high cracking efficiency and of eliminating the trouble with petroleum refinery due to sludge deposit in the case of hydrogenating treating the heavy hydrocarbon oil to cause desulfurization, cracking and the like.

BACKGROUND ART

There is desired in the petroleum refining industry, a petroleum refining technique which is capable of producing a high-quality light petroleum oil in high yield from a low-quality heavy oil as the charge stock as one of the measures for more effectively utilizing the resources.

Nevertheless to the best of the present refining technique, an attempt to enhance cracking efficiency results in deterioration of the petroleum product due to an increase in sulfur content and besides causes the trouble with petroleum refinery due to increasing sludge formation; while an attempt to suppress sulfur content leads to lowered cracking efficiency. Such being the case, there is not available a refining technique satisfying the above-mentioned requirements.

Under such circumstances, a cracking treatment technique which is capable of producing a product oil with a low sulfur content in high cracking efficiency and is free from the formation of sludge is eagerly desired.

As the primary contributor to the trouble with petroleum refinery at the time of high degree of cracking reaction or caused by rise in reaction temperature accompanying the deterioration of a catalyst, sludge formation in the refinery has heretofore greatly taken part therein, sometimes making the operation impossible.

A number of reports are made on the technique which suppresses the formation of sludge in the process directed to a high degree of cracking reaction. However, each of them is nothing but an abstract report failing to elucidate the working effect of the technique.

For example, one two-stage process for hydrogenating a heavy petroleum oil by the use of a hydrogenation catalyst having a large pore diameter of 150 Å or larger in average comprises the first step in which the hydrogenation is carried out at a reaction temperature of 400°C or lower and the second step at a reaction temperature of 400 to 460°C. However, any of the working examples in the above-mentioned disclosure describes the reaction by means of an autoclave only, thus failing to elucidate the extent of decrease in the formation of sludge in a fixed-bed flow type reactor as a commercial production equipment. In addition, it never describes the quality of the hydrogenated product oil. Moreover, the above-disclosed process involves the problem that as compared with the previous direct hydrodesulfurization process, the two-stage

hydrogenation process necessitates a heating furnace facility, thereby being accompanied by increase in the process cost.

The technique of another process relates to a descaling agent which removes the suspended solids such as the scale contained in heavy hydrocarbon oil, a hydrogenation catalyst which removes the dissolved metals such as organometallic compounds in heavy hydrocarbon oil and the methods of using said agent and catalyst, respectively. As the specific method of using, the above-mentioned descaling agent is packed in the forefront of a reactor to prevent catalyst solidification or clogging by scale at the forefront of the reactor.

However, since the sludge that is the object of the present invention is formed on the downstream side of the reactor, the descaling agent is judged to be incapable of exerting the descaling effect.

Aside from the aforestated disclosures, a further process for hydrocracking a heavy oil as the charge stock in which the use of a hydrogenation catalyst in the coexistence of a hydrogen-donative solvent and hydrogen gas is followed by the hydrogenation of the produced oil. According to working examples of this process, although the cracking efficiency is enhanced by the process, the sulfur content in the product oil is still high, thus deteriorating the quality of the product. It is naturally anticipated that the process running cost is raised by the use of the hydrogen-donative agent. Furthermore, the hydrogenation process does not show the effect on decrease in sludge formation, revealing itself to be not so valuable as being expected.

DISCLOSURE OF THE INVENTION

It is an object of the invention to provide a process for hydrogenating a heavy hydrocarbon oil which overcomes or at least reduces one or more disadvantages of the prior art.

According to the present invention, there is provided a process for hydrogenating a heavy hydrocarbon oil including

the successive steps of

(a) hydrogenating-demetalizing a heavy hydrocarbon oil in the presence of hydrogen and a hydrogenating-demetalizing catalyst, to produce a hydrogenated, demetalized oil,

(b) hydrocracking the hydrogenated, demetalized oil from step (a) in the presence of hydrogen and a hydrocracking catalyst to produce a hydrocracked oil, and

(c) hydrodesulfurizing-hydrodenitrifying said hydro-cracked oil from step (b) in the presence of hydrogen and a hydrodesulfurizing-hydrodenitrifying catalyst, said hydrodesulfurizing-hydrodenitrifying catalyst having a pore size distribution as measured by a nitrogen release method in which an average pore diameter of the pores having a diameter of 16 to 1700 Å is from 55 to 90 Å, the volume of the pores having said average pore diameter ±10 Å occupies at least 30% of the volume occupied by the pores having a diameter of 16 to 1,700 Å and the volume of the pores having a diameter of not smaller than 101 Å occupies at most 10% of the volume occupied by the pores having a diameter of 16 to 1,700 Å.

In one embodiment of the invention, there is provided a cracking technique for a heavy hydrocarbon oil which can produce a product oil with a low sulfur content in high cracking efficiency, suppress sludge formation and eliminate operational troubles due to sludge, while overcoming the problems with the conventional processes.

Accordingly, there is provided a process for hydrogenating treatment of a heavy hydrocarbon oil comprising the successive steps of (1) hydrogenating-demetalizing treatment, (2) hydrocracking treatment and (3) hydrodesulfurizing-hydrodenitrifying treatment in the presence of a respective catalyst which process comprises employing in the hydrosulfurizing-hydrodenitrifying treatment, a catalyst having a pore size distribution as measured by nitrogen release method in which an average pore diameter of the pores having a diameter in the range of 16 to 1,700 Å ranges from 55 to 90 Å, the volume of the pores having said average pore diameter

±10 Å occupies at least 30% of the volume occupied by the pores having a diameter in the range of 16 to 1,700 Å and the volume of the pores having a diameter of not smaller than 101 Å occupies at most 10% of the volume occupied by the pores having a diameter in the range of 16 to 1,700 Å.

THE MOST PREFERRED EMBODIMENT TO CARRY OUT THE INVENTION

The charge stock oil as the object of the present invention includes a variety of heavy hydrocarbon oils and is exemplified by residual oil from atmospheric distillation of crude oil, residual oil from vacuum distillation, residual oil from catalytic cracking, oil from visbreaking, tar sand oil and oil shale.

The aforesaid heavy hydrocarbon oil is subjected to hydrogenating treatment in the presence of catalyst comprising the successive steps of (1) hydrogenating-demetalizing treatment, (2) hydrocracking treatment and (3) hydrodesulfurizing-hydrodenitrifying treatment in this order.

In the (1) hydrogenating-demetalizing treatment, a heavy hydrocarbon oil is mixed with hydrogen gas and the resultant mixture is fed to and treated with a hydrogenating-demetalizing treatment equipment, which consists of a single or a plurality of reaction towers. The hydrogenating-demetalizing treatment process and the equipment therefor are exemplified by but not limited to fixed bed, boiling bed, moving bed, upflow system, downflow system and solvent extraction system. In the fixed-bed system, each reaction tower is divided into a plurality of catalyst beds, and a fluid for cooling the reactants is introduced therebetween.

The hydrogenating demetalizing catalyst to be employed in the case of fixed bed may be any of the commercially available demetalizing catalyst comprising at least one metal selected from the group VIA metals, the group VIII metals in the periodic table and compounds thereof (hereinafter metal and metal compound are sometimes abbreviated to "Metal") in the form of oxide, which catalyst is supported on any of a variety of usable carriers exemplified by porous inorganic oxides such as alumina, silica, silica-alumina and sepiolite.

The treatment conditions in the hydrogenating demetalizing treatment may include a reaction temperature of 300 to 450°C (preferably 360 to 420°C); a hydrogen partial pressure of 30 to 200 kg/cm^{2}G, preferably 100 to 180 kg/cm^{2}G; a hydrogen/oil ratio of 300 to 2,000 Nm^3/kℓ, preferably 500 to 1,000 Nm^3/kℓ; and an LHSV (liquid hourly space velocity) of 0.1 to 10 hr^{-1}, preferably 0.3 to 5.0 hr^{-1}.

Thereafter, the effluent oil from the (1) hydrogenating demetalizing treatment process is fed to a (2) hydrocracking treatment equipment, which consists of a single or a plurality of reaction towers. In the case of fixed-bed system, each reaction tower is divided into a plurality of catalyst beds, and a fluid for cooling the reactants is introduced therebetween.

The catalyst to be employed in the hydrocracking treatment is preferably that comprising at least one Metal selected from the group VIA metals and the group VIII metals in the periodic table in the form of oxide, which catalyst is supported on any of a variety of usable carriers such as alumina, silica, alumina-boria, alumina-phosphorus and zeolite. There is also usable a catalyst ~~prepared by the techniques disclosed in~~

which comprises at least one Metal selected from the group VIA metals and the group VIII metals in the periodic table in the form of oxide and which is supported on a carrier consisting of 20 to 80% by weight of an iron-containing zeolite and 80 to 20% by weight of an inorganic oxide. There is further usable a catalyst

which comprises at least one Metal selected from the group VIA metals and the group VIII metals in the periodic table in the form of oxide and which is supported on a carrier consisting of 10 to 90% by weight of an iron-containing zeolite and 90 to 10% by weight of an inorganic oxide. In particular, there is preferably used as the iron-containing zeolite, an iron-containing aluminosilicate obtained by treating a steaming-treated steaming zeolite with an aqueous solution of an iron salt.

The use of the aforesaid iron-containing aluminosilicate is extremely effective in regard to enhancing the cracking efficiency from the distillate with boiling points of not lower than 343°C to the distillate with boiling points of not higher than 343°C.

As the group VIA metal in the periodic table, Mo and W is preferable and as the group VIII metal therein, Ni and Co are preferable.

The treatment conditions in the hydrocracking treatment include a reaction temperature of 300 to 450°C, preferably 380 to 420°C; a hydrogen partial pressure of 30 to 200 kg/cm^{2}G, preferably 100 to 180 kg/cm^{2}G; a hydrogen/oil ratio of 300 to 2,000 Nm^3/kℓ,

preferably 500 to 1,000 $Nm^3/k\ell$; and an LHSV of 0.1 to 2.0 hr^{-1}, preferably 0.2 to 1.0 hr^{-1}.

As the result of the above-mentioned hydrocracking treatment, a high-quality naphtha distillate and kerosene/gas-oil distillates can be obtained in high efficiency by cracking a distillate of not lower than 343°C to a distillate of not higher than 343°C.

The effluent oil from the (2) hydrocracking treatment step preceded by the (1) hydrogenating demetalizing treatment step is fed to a (3) hydrosulfurizing hydrodenitrifying treatment equipment, which consists of a single or a plurality of reaction towers. In the case of fixed-bed system, each reaction tower is divided into a plurality of catalyst beds, and a fluid for cooling the reactants is introduced therebetween.

The catalyst to be employed in the hydrodesulfurizing and hydrodenitrifying treatment is greatly different from the conventional hydrodesulfurization catalysts that have heretofore been used in hydrodesulfurization and thus, constitutes the feature of the present invention.

Prior to investigation on the present hydrodesulfurization catalyst, sludge forming mechanism was investigated and elucidated by the present inventors. As a result, it has been proved that asphaltene (n-heptane-insoluble and toluene-soluble component) which is one of the high molecular components in the charge stock oil is greatly changed in its primary and supermolecular structures and converted into sludge by treating the oil under severe conditions. It follows from the aforestated fact that in producing a product oil with a low sulfur content in high cracking efficiency, the sludge formation is

suppressed by the application of the catalyst capable of restricting the asphaltene cracking to a more mild level which comprises at least one metal component selected from the group consisting of the group VIA metals and the group VIII metals in the periodic table, specifically exemplified by Co-Mo and Ni-Mo in the form of oxide, which catalyst is supported in an amount of 8 to 20% by weight expressed in terms of oxide on any of a variety of usable carriers such as alumina, silica, alumina-silica, alumina-boria, alumina-phosphorus, zeolite and mixtures thereof and which catalyst has a pore size distribution as measured by nitrogen release method in which an average diameter of the pores having a diameter of 16 to 1,700 Å ranges from 55 to 90 Å, the volume of the pores having said average pore diameter ±10 Å occupies at least 30% of the volume occupied by the pores having a diameter of 16 to 1,700 Å and the volume of the pores having a diameter larger than 101 Å occupies at most 10% of the volume occupied by the pores having a diameter of 16 to 1,700 Å. In particular, the use of alumina-boria or alumina-phosphorus as the carrier exhibits a remarkable effect. The alumina-boria as the carrier has preferably a boria content of 5 to 30% by weight, and the alumina-phosphorus as the carrier has preferably a phosphorus content of 1 to 10% by weight.

The above-described trouble with petroleum refinery due to sludge formation is publicly known from the various existing literatures and routine commercial operation of the refinery, and the sludge amount is quantified as toluene-insolubles.

The treatment conditions in the hydrodesulfurizing hydrodenitrifying treatment include a reaction temperature of 300 to

450°C, preferably 360 to 420°C; a hydrogen partial pressure of 30 to 200 kg/cm^{2}G, preferably 100 to 180 kg/cm^{2}G; a hydrogen/oil ratio of 300 to 2,000 Nm^3/kℓ, preferably 500 to 1,000 Nm^3/kℓ; and an LHSV of 0.1 to 2.0 hr^{-1}, preferably 0.1 to 0.5 hr^{-1}.

As the result of the above-mentioned hydrodesulfurizing hydrodenitrifying treatment, the distillate of not lower than 343°C boiling point is improved in particular.

Moreover, the combined use of the aforestated catalyst in the (3) hydrodesulfurizing hydrodenitrifying treatment and the iron-containing aluminosilicate obtained by treating a steaming-treated zeolite with an aqueous solution of an iron salt in

the (2) hydrocracking treatment enables the product oil with a low sulfur content to be produced more efficiently in high cracking efficiency without equipment trouble due to sludge formation.

In each of the treatment steps comprising the (1) hydrogenating demetalizing treatment, (2) hydrocracking treatment and (3) hydrodesulfurizing hydrodenitrifying treatment, a heavy hydrocarbon oil with sulfur content of 1.0% or less by weight in the distillate of not lower than 343°C boiling point can be obtained in a cracking efficiency of 20% or higher, preferably 20 to 70% by weight in terms of the distillate of not lower than 343°C boiling point contained in the charge stock oil by optionally varying the inlet temperature in the range of 300 to 420°C.

The effluent oil discharged from the reaction process comprising the above (1), (2) and (3) treatments is usually introduced in a separation step according to the conventional method, where it is

separated into gas portion and liquid portion by being treated with a plurality of separation vessels. The gas portion is subjected to the step of removing hydrogen sulfide, ammonia, etc., followed by the step of enhancing hydrogen purity, etc. and is recycled through the reaction process together with a fresh hydrogen feed gas.

On the other hand, the liquid portion which has been separated in the separation step is introduced in a distillation step, where it is distilled or separated into respective fractions according to the conventional method. Specifically, it can be separated into naphtha fraction, kerosene fraction, gas oil fraction and residuum fraction by setting the fractionating conditions under atmospheric fractionation, for example, on 145 to 190°C for naphtha cut temperature, 235 to 265°C for kerosene cut temperature, 343 to 380°C for gas oil cut temperature and 380°C and higher for residuum cut temperature. The naphtha fraction thus obtained is used as the charge stock oil for a catalytic reformer so that a reformed gasoline with a high octane value can be produced. The distillating fractionation may be carried out by vacuum distillation.

As described hereinbefore, in hydrogenating treatment of a heavy hydrocarbon oil, a product oil with a low sulfur content can be produced in high cracking efficiency without operational trouble while sludge formation is suppressed by using a catalyst for hydrodesulfurizing and hydrodenitrifying treatments, the pore size distribution of which catalyst is restricted to a specific range.

Accordingly, the process according to the present invention is advantageous in that:

(1) Long-term stable operation is possible, thus curtailing running

cost.

(2) It is possible to select charge stock oil in a wide range from light hydrocarbon oil to heavy hydrocarbon oil.

(3) High profitability is assured by virtue of high cracking efficiency and high quality of the product.

(4) It is possible to select the cracking efficiency from low to high, thereby imparting flexibility to the process equipment constitution.

Consequently, the present invention establishes a surpassingly excellent cracking treatment technique for a heavy hydrocarbon oil from the viewpoint of effective utilization of resources, and is expected to find commercial applications.

In the following, the present invention will be described in more detail with reference to examples and comparative examples. In the examples and comparative examples, the residuum having the following properties obtained from atmospheric distillation of the Arabian heavy oil was used as the heavy hydrocarbon oil, that is, the charge stock oil.

Properties:

Specific gravity	0.9798
Kinematic viscosity (at 50°C)	2,018 cSt
Sulfur content	4.13% by weight
Nitrogen content	2500 ppm
Vanadium content	85 ppm
Nickel content	36 ppm
Carbon residue	15% by weight
Asphaltene	7.7% by weight

Initial boiling point	281°C		
Distillation range	-	341°C	5%
	-	376°C	10%
	-	460°C	30%
	-	546°C	50%

Example 1

1) Hydrogenation catalyst

① Hydrogenation-demetalization catalyst

α-alumina carrier,

1.5% by weight of molybdenum oxide, 3% by weight of nickel oxide, 3% by weight of vanadium oxide

② Hydrocracking catalyst

Alumina carrier with 65% by weight of iron-containing zeolite (the carrier prepared according to Example 1 in Japanese Patent Application Laid-Open No. 289419/1990)

4% by weight of cobalt oxide, 10% by weight of molybdenum oxide.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina-boria carrier (2.4% by weight of boria), 8.8% by weight of molybdenum oxide, 3.4% by weight of cobalt oxide.

The catalyst had a pore distribution as measured by nitrogen release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 85 Å, the volume of the pores having 85 ±10 Å occupied 39% of the volume occupied by the pores having 16 to 1,700 Å and the volume of the pores having a diameter of not smaller than 101 Å occupied 6% of the volume occupied by the pores

having 16 to 1,700 Å diameter.

2) Hydrogenation treatment conditions

Treatment temperature	390 to 410°C
Hydrogen partial pressure	145 kg/cm^{2}G
Hydrogen/oil ratio	860 Nm^3/kℓ

A 1 liter fixed-bed reactor was packed with 21% by volume of the hydrogenation demetalization catalyst, 36% by volume of the hydrocracking catalyst and 43% by volume of the hydrodesulfurization hydrodenitrification catalyst each as described above, in this order and was used to treat the rediuum from atmospheric distillation of the Arabian heavy oil under the above-mentioned treatment conditions at a downflow rate of 314 cc/hr. The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 382°C, respectively.

Comparative Example 1

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to the types of the hydrogenation-demetalization catalyst and the hydrocracking catalyst and the volumetric proportion of each catalyst in combination, but the under-mentioned hydrodesulfurization-hydrodenitrification catalyst was employed.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina carrier, 6.9% by weight of molybdenum oxide, 1.2% by weight of cobalt oxide, 0.7% by weight of nickel oxide.

The catalyst had a pore distribution as measured by nitrogen release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 118 Å, the volume of the pores having 118 ±10 Å diameter occupied 31 4% of the volume occupied by the pores having 16 to 1,700 Å diameter and the volume of the pores having a diameter of not smaller than 101 Å occupied 51% of the volume occupied by the pores having 16 to 1,700 Å diameter.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 382°C, respectively.

Example 2

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to three types of the catalysts and volumetric proportion of each catalyst in combination.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

Example 3

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to the types of the hydrogenation-demetalization catalyst and the hydrocracking catalyst and the volumetric proportion of each catalyst in combination, but the under-mentioned hydrodesulfurization-hydrodenitrification catalyst was employed.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina-boria carrier (2.6% by weight of boria), 9.2% by weight of molybdenum oxide, 3.5% by weight of cobalt oxide.

The catalyst had a pore distribution as measured by nitrogen release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 59 Å, the volume of the pores having 59 ±10 Å diameter occupied 50% of the volume occupied by the pores having 16 to 1,700 Å diameter and the volume of the pores having a diameter of not smaller than 101 Å occupied 2.2% of the volume occupied by the pores having 16 to 1,700 Å diameter.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

Example 4

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to the types of the hydrogenation-demetalization catalyst and the hydrocracking catalyst and the volumetric proportion of each catalyst in combination, but the under-mentioned hydrodesulfurization-hydrodenitrification catalyst was employed.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina-phosphorus carrier (2.1% by weight of phosphorus), 9.3% by weight of molybdenum oxide, 3.6% by weight of cobalt oxide.

The catalyst had a pore distribution as measured by nitrogen

release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 83 Å, the volume of the pores having 83 ±10 Å diameter occupied 37% of the volume occupied by the pores having 16 to 1,700 Å diameter and the volume of the pores having a diameter of not smaller than 101 Å occupied 7% of the volume occupied by the pores having 16 to 1,700 Å diameter.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

Comparative Example 2

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Comparative Example 1 with regard to three types of the catalyst and volumetric proportion of each catalyst in combination.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

Comparative Example 3

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to the types of the hydrogenation-demetalization catalyst and the hydrocracking catalyst and the volumetric proportion of each catalyst in combination, but the under-mentioned hydrodesulfurization-hydrodenitrification catalyst was employed.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina-boria carrier (2.2% by weight of boria), 8.6% by weight of molybdenum oxide, 3.3% by weight of cobalt oxide.

The catalyst had a pore distribution as measured by nitrogen release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 110 Å, the volume of the pores having 110 ±10 Å diameter occupied 11.3% of the volume occupied by the pores having 16 to 1,700 Å diameter and the volume of the pores having a diameter of not smaller than 101 Å occupied 47% of the volume occupied by the pores having 16 to 1,700 Å diameter.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

To evaluate the performance of the product oil obtained in each of the examples and comparative examples, measurements were made of toluene-insoluble portion, sulfur content and cracking efficiency of the fraction with a boiling point of 343°C or higher for each of the product oils. The results are given in Table 1.

Comparative Example 4

The charge stock oil was subjected to hydrogenating treatment in the same manner as in Example 1 with regard to the types of the hydrogenation-demetalization catalyst and the hydrocracking catalyst and the volumetric proportion of each catalyst in combination, but the under-mentioned hydrodesulfurization-hydrodenitrification catalyst was employed.

③ Hydrodesulfurization-hydrodenitrification catalyst

γ-alumina-phosphorus carrier (2.2% by weight of phosphorus), 8.7% by weight of molybdenum oxide, 3.2% by weight of cobalt oxide.

The catalyst had a pore distribution as measured by nitrogen release method in which an average pore diameter of the pores having 16 to 1,700 Å diameter was 105 Å, the volume of the pores having 105 ±10 Å diameter occupied 10.5% of the volume occupied by the pores having 16 to 1,700 Å diameter and the volume of the pores having a diameter of not smaller than 101 Å occupied 45% of the volume occupied by the pores having 16 to 1,700 Å diameter.

The reaction temperatures in the hydrogenation-demetalization catalyst bed, hydrocracking catalyst bed and hydrodesulfurization-hydrodenitrification catalyst bed were 380°C, 405°C and 392°C, respectively.

To evaluate the performance of the product oil obtained in each of the examples and comparative examples, measurements were made of toluene-insoluble portion, sulfur content and cracking efficiency of the fraction with a boiling point of 343°C or higher for each of the product oil. The results are given in Table 1.

Table 1

	Toluene-insoluble rate (% by weight)	Cracking efficiency of fraction with ≥ 343°C boiling points (% by weight)	Sulfur content in product oil (% by weight)
Example 1	≤ 0.005	63.8	0.100
Comparative Example 1	0.01	62.1	0.173
Example 2	≤ 0.005	64.5	0.090
Example 3	≤0.005	63.5	0.100
Example 4	≤0.005	64.0	0.092
Comparative Example 2	0.017	61.6	0.140
Comparative Example 3	0.020	63.1	0.100
Comparative Example 4	0.019	62.0	0.130

In the present invention, cracking efficiency and product oil are defined as follows, respectively, and were measured by the method described hereunder.

The term "cracking efficiency" is used to quantitatively indicate the extent of conversion of an oil fraction having boiling points of not lower than 343°C into an oil fraction having boiling points of not higher than 342°C. An oil fraction having boiling points of not lower than 343°C is made into an oil fraction with a high value added which can be used for automobile engines, jet engines, diesel engines, etc. by being converted into an oil fraction having boiling points of not higher than 342°C. Therefore, a catalyst which causes high cracking

efficiency is highly rated. The term "product oil" expresses the oil fraction having at least 5 carbon atoms which is obtained at the outlet of the last reaction tower.

1) Cracking efficiency

Cracking efficiency = [% by weight of oil fraction having boiling points of not lower than 343°C in charge stock oil - (% by weight of oil fraction having boiling points of not lower than 343°C in product oil × liquid recovery rate)] / % by weight of oil fraction having boiling points of not lower than 343°C.

2) Toluene-insoluble rate

An oil fraction having boiling points of not lower than 343°C was obtained from a product oil with a vacuum distillation plant. Then, to the resultant oil fraction was added 20 times by volume of toluene with heating at 80°C for 1 hour. Subsequently, the mixture was filtered with a filter having 1 μm pore size, the filter cake caught on the filter was weighed, and toluene-insoluble rate was calculated by the following formula

Toluene insoluble rate (% by weight) = [weight of filter cake (g) / amount of charged oil fraction having boiling points of not lower than 343°C (g)] × 100

The weight of filter cake was obtained by means of a filter made to have a constant weight in advance from the difference between the weight of the filter before filtration and the weight thereof after filtration.

As can be seen from Table 1, the product oils in the examples are superior to those in the comparative examples with regard to the cracking efficiency of fraction with ≥ 343°C boiling points, sulfur

content in product oil and especially, toluene-insoluble rate.

INDUSTRIAL APPLICABILITY

As described above, according to the hydrogenating treatment of heavy hydrocarbon oil of the present invention, a product oil with a low sulfur content can be produced in high cracking efficiency without operational trouble while sludge formation is suppressed by using a catalyst for hydrodesulfurizing and hydrodenitrifying treatment, the pore size distribution of which catalyst is restricted to a specific range.

Accordingly, the present invention establishes a surpassingly excellent cracking treatment technique for a heavy hydrocarbon oil from the viewpoint of effective utilization of resources, and is expected to find commercial applications.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for hydrogenating a heavy hydrocarbon oil including the successive steps of

(a) hydrogenating-demetalizing a heavy hydrocarbon oil in the presence of hydrogen and a hydrogenating-demetalizing catalyst, to produce a hydrogenated, demetalized oil,

(b) hydrocracking the hydrogenated, demetalized oil from step (a) in the presence of hydrogen and a hydrocracking catalyst to produce a hydrocracked oil, and

(c) hydrodesulfurizing-hydrodenitrifying said hydrocracked oil from step (b) in the presence of hydrogen and a hydrodesulfurizing-hydrodenitrifying catalyst, said hydrodesulfurizing-hydrodenitrifying catalyst having a pore size distribution as measured by a nitrogen release method in which an average pore diameter of the pores having a diameter of 16 to 1700 Å is from 55 to 90 Å, the volume of the pores having said average pore diameter ±10 Å occupies at least 30% of the volume occupied by the pores having a diameter of 16 to 1,700 Å and the volume of the pores having a diameter of not smaller than 101 Å occupies at most 10% of the volume occupied by the pores having a diameter of 16 to 1,700 Å.

2. A process for hydrogenating a heavy hydrocarbon oil according to claim 1, wherein said hydrogenating-demetalising, said hydrocracking and said hydrodesulfurising-hydrodenitrifying steps are conducted at a reaction temperature of 300 to 450°C, a hydrogen partial pressure of 30 to 200 kg/cm^2G and a hydrogen/oil ratio of 300 to 2,000 Nm^3/kl.

3. The process according to Claim 1 or Claim 2 wherein the catalyst employed in the hydrocracking includes a metal belonging to group VIA of the periodic table and a metal belonging to group VIII of the periodic table or a compound thereof supported on a carrier having 10 to 90%

by weight of iron-containing zeolite and 90 to 10% by weight of an inorganic oxide.

4. The process according to any one of Claims 1 to 3 wherein the catalyst employed in the hydrodesulfurizing-hydrodenitrifying includes a metal belonging to group VIA in the periodic table and a metal belonging to group VIII in the periodic table in a total amount of 8 to 20% by weight expressed in terms of the metal oxide, which metals are supported on an alumina-boria carrier containing 5 to 30% by weight of boria.

5. The process according to any one of the Claims 1 to 3 wherein the catalyst employed in the hydrodesulfurizing-hydrodenitrifying includes a metal belonging to group VIA of the periodic table and a metal belonging to group VIII of the periodic table in a total amount of 8 to 20% by weight expressed in terms of the metal oxide, which metals are supported on an alumina-phosphorus carrier containing 1 to 10% by weight of phosphorus.

6. The process according to any one of Claims 1 to 4 wherein a cracking efficiency which indicates the extent of conversion of an oil fraction having a boiling point of not lower than 343^{o}C, is 20% by weight or higher, and the sulfur content in the product oil is 1.0% by weight or lower.

7. The process according to any one of Claims 1 to 6 wherein the hydrogenating-demetalizing is carried out at a temperature of 360 to 420^{o}C, a hydrogen partial pressure of 100 to 180 kg/cm^{2}G, a hydrogen/oil ratio of 500 to 1,000 Nm^{3}/kl and a liquid hourly space velocity of 0.1 to 10 hr^{-1}; the hydrocracking is carried out at a temperature of 380 to 420^{o}C, a hydrogen partial pressure of 100 to 180 kg/cm^{2}G, a hydrogen/oil ratio of 500 to 1,000 Nm^{3}/kl and a liquid hourly space velocity of 0.1 to 20 hr^{-1}; and the hydrodesulfurizing-hydrodenitrifying is carried out at a temperature of 360 to 420^{o}C, a

hydrogen partial pressure of 100 to 180 kg/cm^2G, a hydrogen/oil ratio of 500 to 1,000 Nm^3/kl and a liquid hourly space velocity of 0.1 to 2.0 hr^{-1}.

8. The process according to Claim 7 wherein the hydrogenating-demetalizing is carried out at liquid hourly space velocity of 0.3 to 5.0 hr^{-1}; the hydrocracking is carried out at a liquid hourly space velocity of 0.2 to 1.0 hr^{-1}; and the hydrosulfurizing-hydrodenitrifying is carried out at a liquid hourly space velocity of 0.1 to 0.5 hr^{-1}.

9. The process according to any one of Claims 3 to 8 wherein the metal belonging to group VIA of the periodic table is Mo and the metal belonging to group VIII of the periodic table is at least one metal selected from the group consisting of Co and Ni.

10. The process according to any one of Claims 1 to 9 wherein the catalyst employed in the hydrogenating-demetalizing includes at least one metal selected from a group VIA metal of the periodic table, a group VIII metal of the periodic table, and compounds thereof in the form of an oxide, said metal being supported on a porous inorganic oxide carrier selected from the group consisting of alumina, silica, silica-alumina and sepiolite.

11. The process according to Claim 10, wherein the group VIA metal is Mo and the group VIII metal is Co or Ni.

12. A process for hydrogenating a heavy hydrocarbon oil into a product oil, substantially as herein described with reference to any one of Examples 1 to 4.

DATED: 24 October 1994
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IDEMITSU KOSAN CO., LTD.

ABSTRACT OF THE DISCLOSURE

There is disclosed a process for hydrogenating treatment of a heavy hydrocarbon oil comprising the successive steps of (1) hydrogenating-demetalizing treatment, (2) hydrocracking treatment and (3) hydrodesulfurizing-hydrodenitrifying treatment in the presence of respective catalysts which process comprises employing in the hydrodesulfurizing-hydrodenitrifying treatment, a catalyst having a pore size distribution restricted to a specific range as measured by nitrogen release method. According to the above-mentioned process, a product oil with a low sulfur content can be obtained in high cracking efficiency from a heavy hydrocarbon oil without equipment trouble due to sludge formation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00203

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 C10G65/12, C10G45/04, C10G45/08, C10G45/12, C10G47/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^5 C10G65/12, C10G45/04, C10G45/08, C10G45/12, C10G47/20

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 58-112049 (Catalysts & Chemical Industries Co., Ltd.), July 4, 1983 (04. 07. 83), (Family: none)	1-5
Y	JP, A, 54-23096 (Exxon Research & Engineering Co.), February 21, 1979 (21. 02. 79), & DE, A, 2730698 & GB, A, 1584706	1-5
Y	JP, B1, 47-44001 (Director General, Agency of Industrial Science and Technology), November 7, 1972 (07. 11. 72), (Family: none)	1-5
A	US, A, 3472759 (Atlantic Richfield Co.), October 14, 1969 (14. 10. 69), (Family: none)	1-5
A	US, A, 3686093 (Robert Leafd Irvine), August 22, 1972 (22. 08. 72), & GB, A, 1342061	1-5

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
May 10, 1993 (10. 05. 93)	June 8, 1993 (08. 06. 93)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00203

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3050459 (Hydrocarbon Research Inc. Corp.), August 21, 1962 (21. 08. 62), (Family: none)	1-5
A	JP, A, 47-33103 (Arugen & Maunt Prospect Rose U.O.P. Plaza), November 17, 1972 (17. 11. 72), & DE, A, 2212123 & FR, A, 2130297	1-5
A	JP, A, 47-12979 (Texaca Development Corp.), June 30, 1972 (30. 06. 72), & DE, A, 216449 & FR, A, 2120022 & US, A, 3716476	1-5
A	JP, A, 2-289419 (Research Association For Residual Oil Processing), November 29, 1990 (29. 11. 90), & EP, A, 384186 & US, A, 5141737	2

国際調査報告	国際出願番号 PCT/JP 93 / 00203

A. 発明の属する分野の分類（国際特許分類（IPC））

Int. Cl⁵ C10G65/12, C10G45/04, C10G45/08, C10G45/12, C10G47/20

B. 調査を行った分野

調査を行った最小限資料（国際特許分類（IPC））

Int. Cl⁵ C10G65/12, C10G45/04, C10G45/08, C10G45/12, C10G47/20

最小限資料以外の資料で調査を行った分野に含まれるもの

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

C. 関連すると認められる文献

引用文献のカテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求の範囲の番号
Y	JP, A, 58-112049（触媒化成工業株式会社）, 4. 7月. 1983（04. 07. 83）（ファミリーなし）	1-5
Y	JP, A, 54-23096（エクソン・リサーチ・エンド・エンジニアリング・コンパニー）, 21. 2月. 1979（21. 02. 79） &DE, A, 2730698&GB, A, 1584706	1-5
Y	JP, B1, 47-44001（工業技術院長）,	1-5

☑ C欄の続きにも文献が列挙されている。　☐ パテントファミリーに関する別紙を参照。

* 引用文献のカテゴリー
「A」特に関連のある文献ではなく、一般的技術水準を示すもの
「E」先行文献ではあるが、国際出願日以後に公表されたもの
「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「O」口頭による開示、使用、展示等に言及する文献
「P」国際出願日前で、かつ優先権の主張の基礎となる出願の日の後に公表された文献
「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
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「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの
「&」同一パテントファミリー文献

国際調査を完了した日	国際調査報告の発送日
10. 05. 93	08.06.93

名称及びあて先	特許庁審査官（権限のある職員）
日本国特許庁（ISA/JP） 郵便番号100 東京都千代田区霞が関三丁目4番3号	岩瀬眞紀子 印　4H 2115 電話番号 03-3581-1101 内線 3444

様式PCT/ISA/210（第2ページ）（1992年7月）

C（続き）．　関連すると認められる文献

引用文献のカテゴリー*	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求の範囲の番号
	7．11月．1972（07．11．72）（ファミリーなし）	
A	US，A，3472759（Atlantic Richfield Co.），14．10月．1969（14．10．69）（ファミリーなし）	1－5
A	US，A，3686093（Robert Leafd Irvine），22．8月．1972（22．08．72）&GB，A，1342061	1－5
A	US，A，3050459（Hydrocarbon Research Inc，Corp．），21．8月．1962（21．08．62）（ファミリーなし）	1－5
A	JP，A，47－33103（アルゴンクイン アンド マウント プロスペクト ローズ・ユーオーピー プラザ）17．11月．1972（17．11．72）&DE，A，2212123&FR，A，2130297	1－5
A	JP，A，47－12979（テキサコ デイベロップメント コーポレーション），30．6月．1972（30．06．72）&DE，A，216449&FR，A，2120022&US，A，3716476	1－5
A	JP，A，2－289419（重質油対策技術研究組合），29．11月．1990（29．11．90）&EP，A，384186&US，A，5141737	2