

Process and apparatus for the demetallization of a hydrocarbon oil

The invention relates to a process for the demetallization of a hydrocarbon oil by passing said oil together with hydrogen over one or more fixed beds of a demetallization catalyst.

When refining hydrocarbon oils, such as mineral oils and in particular petroleum, the light products are usually first removed by distillation at atmospheric pressure, subsequently heavier fractions are separated off by means of vacuum distillation and the remaining residue (short residue) is deasphalted, in which process deasphalted vacuum residue of a mineral oil (also referred to as DAO below) and asphalt are obtained. The heavier fractions obtained in the vacuum distillation (also referred to as vacuum distillate fractions) and the residual fractions, in particular DAO, can be used as heavy fuel or as feedstock for catalytic cracking. In order to discharge the smallest possible quantity of sulphur compounds into the atmosphere during the combustion of heavy fuel, it is necessary that the sulphur content of oils to be used as heavy fuel should be as low as possible. To this end the sulphur is very suitably removed with catalysts suitable therefor in the presence of hydrogen. Said catalysts are deactivated rapidly if the fraction to be desulphurized contains a considerable quantity of metal.

If the DAO and/or vacuum distillate fractions are to be used as feed for a catalytic cracking reaction, the metal content and the tendency to coke deposition of the feed to be used must be as low as possible in order to prevent rapid deactivation of the cracking catalyst.

In order to meet the requirements set for the metal content, at least part of the metals, which occur in larger quantities in residual fractions than in the vacuum distillate fractions, must therefore in many cases be removed both from vacuum distillate fractions and from residual fractions (by which are meant fractions which have remained behind as residue in the vacuum distillation of a mineral oil or have been obtained from such a residue, for example short residue, DAO, asphalt). Said metals consist for the greater part of nickel and vanadium, which may occur in considerable quantities in mineral oils. Removal of metals, which need not be complete, is referred to as demetallization in the present application.

The usual catalysts for catalytic hydrodesulphurization are not resistant to quantities of metals in the feed in excess of about 20 ppmw, since in the case of larger quantities of metal unacceptable pressure drop across the catalyst occurs after a relatively short time. For this reason hydrocarbon oils having a metal content higher than about 20 ppm cannot be desulphurized with said catalysts in an economically justified manner.

In a number of cases it is therefore advisable

that prior to desulphurization a hydrocarbon oil to be desulphurized should be demetallized to a metal content below about 20 ppm, and this applies in particular to residual fractions, since the latter usually have metal contents which are considerably higher than 20 ppm.

For the demetallization of hydrocarbon oils in the presence of hydrogen (hydro-demetallization) specific catalysts exist which possess a high activity for demetallization but only a low capacity for desulphurization. Consequently, the hydrocarbon oil obtained in the demetallization will in many cases still have to be desulphurized, in order to obtain the desired demetallized and desulphurized hydrocarbon oils. The hydrodesulphurization is very suitably carried out by means of catalysts suitable therefore which as stated above, are not resistant to quantities of metal in the feed of about 20 ppm or more.

If no special measures are taken, demetallization catalysts have a relatively short life, since after a relatively short time, as a result of the quantities of metals and coke which originate from the hydrocarbon oil and have been deposited on the catalyst, the catalyst is deactivated and such a high pressure drop across the demetallization catalyst occurs that said catalyst cannot be used further and must be removed and/or regenerated.

It is possible to use a fresh quantity of demetallization catalyst which is contained, for example, in a different parallel-connected reactor than the deactivated catalyst and to regenerate and/or remove the deactivated demetallization catalyst.

However, this method, has the drawback that for the regeneration and/or removal from the reactor of the deactivated demetallization catalyst this reactor must be opened or at least the hydrogen present therein must be replaced by air. On a site where a number of reactors are located in which hydrotreatments at high pressure and temperature are carried out, it is, for safety reasons, undesirable to shut down one of the reactors separately and replace the hydrogen therein by an oxygen-containing gas. The aim will be to close down the whole plant simultaneously for the regeneration and/or removal of the demetallization catalyst.

The invention provides a process for the hydrodemetallization of a hydrocarbon oil, in which process the time during which a demetallization catalyst can be used without it being necessary to be removed and/or regenerated, is prolonged considerably.

It is known from US—A—3206395 to introduce a stove oil between the middle and bottom catalyst beds present in a desulphurization reactor whilst passing downwardly hydrogen-rich gases over a first catalyst mass which is thus prevented from being contaminated with

vapors of the stove oil feed. No reference is made at all, however, that the life of a demetallization catalyst could be prolonged considerably by moving the point of supply of the hydrocarbon oil downstream after a first catalyst bed has been deactivated.

Accordingly, the invention relates to process for the demetallization of a hydrocarbon oil by passing said oil together with hydrogen over one or more fixed beds of a demetallization catalyst, which process is characterized in that whenever that catalyst portion which is first contacted with the hydrocarbon oil is deactivated the point of supply of the hydrocarbon oil is moved downstream, at least part of the original supply of hydrogen being maintained over the entire catalyst.

It is essential that at least part of the hydrogen stream should be maintained over the entire catalyst. After the supply of the hydrocarbon oil to be demetallized has been moved to a point located further downstream, a quantity of oil invariably remains present on the deactivated part of the catalyst. This oil may exhibit undesired decomposition reactions with heat production, as a result of which local overheating of the deactivated catalyst may occur. By maintaining a hydrogen stream over the entire catalyst such reactions are largely suppressed and if they nevertheless occur, removal of the heat produced is ensured.

In addition to the hydrogen stream maintained over the entire catalyst it is as a matter of course, possible to introduce hydrogen in one or more downstream places if desired. The moment when the catalyst portion which is first contacted with the oil to be demetallized is considered deactivated, is determined by the pressure drop occurring across the catalyst. Depending on the conditions a not excessive pressure drop may be permitted before the supply of hydrocarbon oil is removed. When under the prevailing conditions the period of time elapsing between the supply of hydrocarbon oil to a certain part of the catalyst and the deactivation thereof has become known, it is of course also possible on the basis of said period to move the supply of hydrocarbon oil to a point located further downstream a short time before the pressure drop across the catalyst becomes unacceptable.

Any hydrocarbon oil to be demetallized can serve as feed for the process according to the invention. As examples may be mentioned crude oil, oil from which the volatile products are removed (topped crude oil), oil from which light products are removed by distillation at atmospheric pressure (so-called long residue), shale oils, oils obtained from tar sands. Preference is given to residual fractions, as defined above.

Demetallization catalysts are known; they usually consist of oxidic carriers on which one or more metals with hydrogenation activity (or compounds of said metals) are optionally

deposited. In the process according to the invention use is very suitably made of catalysts of the type described in the Dutch patent application 7309387. Said catalysts contain one or more metals with hydrogenation activity on a carrier and fulfil the following requirements:

- 1) $p/d > 3.5-0.02 v$, in which p represents the specific average pore diameter in nm, d represents the specific average particle diameter in mm and v is the percentage of the total pore volume consisting of pores having a diameter above 100 nm,
- 2) the total pore volume is above 0.40 ml/g,
- 3) v is below 50 and
- 4) the specific surface area is above 100 m²/g; in case the catalyst has such a p and d that the quotient p/d is higher than 3.5-0.02 v , but at most 10-0.15 v , the catalyst must fulfil the following additional requirements:
 - a) the nitrogen pore volume is above 0.60 ml/g,
 - b) the specific surface area is about 150 m²/g and
 - c) p is above 5 nm.

The values to be used for p , d , v , the total pore volume, the nitrogen pore volume and the specific surface area must be determined as described in the Dutch patent application 7309387.

The catalyst contains very suitably, metals with hydrogenation activity selected from the group consisting of nickel, cobalt, molybdenum, vanadium and tungsten, and particularly preference is given to catalysts which contain at least one metal of the group consisting of nickel and cobalt and at least one metal of the group consisting of molybdenum, vanadium and tungsten. Catalysts containing nickel and vanadium are particularly suitable. The metals are preferably present as their oxides or sulphides.

Alumina and silica-alumina are very suitable as carriers. Preference is given to carriers completely or substantially completely consisting of silica.

Very suitable catalysts for the hydro-demetalization according to the invention are those described in the Dutch patent application 7316396. Said catalysts contain 0.1-15 parts by weight of the metal combination nickel-vanadium per 100 parts by weight of a silica carrier and have a loss on ignition, determined under standard conditions, of less than 0.5% by weight.

Catalysts as described in the Dutch patent application 7412155 are also very suitable. The latter catalysts fulfil the above-mentioned requirements and are obtained by the nodulizing technique; they have a pore volume, present in pores having a diameter above 50 nm, of at least 0.2 ml/g.

If the hydrocarbon oil to be demetallized has

a high metal content, it is also possible to use as catalyst silica on which no metals with hydrogenation activity have been deposited, as described in the Dutch patent application 7607552.

The process according to the invention is carried out under conditions which are usual for hydrodemetallization. The hydrocarbon oil to be demetallized (which in most cases is for at least 80 vol.% in the liquid phase) together with hydrogen is very suitably passed in downward direction over the catalyst at a temperature between 300 and 450°C (preferably between 350 and 425°C), a total pressure between 75 and 250 bar (preferably between 100 and 200 bar), a hydrogen partial pressure between 35 and 120 bar (preferably between 50 and 100 bar), a space velocity of 0.1—25 parts by volume of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 100—2000 (preferably 200—1500) N1 of H₂/kg of feed.

The hydrogen required for the hydrodemetallization may be a hydrogen containing gas stream, such as a reformer off-gas stream, or a mainly pure hydrogen. The hydrogen-containing gases preferably contain at least 60% by volume of hydrogen.

The demetallization catalyst may be present in one fixed bed, but is preferably present in several serially connected fixed beds. The fixed beds can be located in one or more reactors. The size of the catalyst beds is very suitably so chosen that the supply point of hydrocarbon oil to be demetallized is moved to a place between an exhausted catalyst bed and the next fresh catalyst bed.

After the furthest downstream portion of the catalyst is also deactivated, the catalyst must be taken out of service and can be regenerated and/or removed. During regeneration the coke deposits and the metal deposits (which in many cases mainly consist of vanadium and to a lesser extent of nickel) must be at least partly removed. The regeneration is very suitably carried out by the methods described in the Dutch patent applications 7511993, 7703181 and 7703180. In these methods, the deactivated catalyst is extracted with an aqueous solution of a mineral acid (for example sulphuric acid), which extraction is very suitably preceded by a treatment with a reducing agent or is carried out in the presence of a reducing agent. Sulphur dioxide is very suitable as reducing agent.

In order to remove also the coke and sulphur deposits it is advisable, before the extraction with an aqueous solution of a mineral acid (and the optional treatment with a reducing agent), to subject the deactivated catalyst to a treatment with steam, and/or an oxygen-containing gas such as air, and/or with a mixture of steam and air, at a temperature above 250°C at atmospheric or a higher pressure.

If the carrier of the catalyst is resistant to an

aqueous solution of mineral acid (i.e. consists of, for example, silica) the catalyst can be reused after removal of the coke, sulphur and metals, optionally after application of the above-mentioned metals with hydrogenation activity.

If the carrier is not resistant to an aqueous solution of a mineral acid (i.e. consists, for example, of alumina) regeneration in the above-mentioned manner is impossible. In that case it is also possible, however, to carry out the treatment with mineral acid in order to recover the metals deposited from the hydrocarbon oil. Said metals can of course also be recovered from the extract obtained in the treatment with an aqueous mineral acid solution of deactivated catalysts, the carriers of which are resistant to a treatment of this type.

The demetallized hydrocarbon oil obtained in the process according to the invention can be used for any desired purpose. The demetallization need of course not be complete and a quantity of metal may still be present in the demetallized product.

As stated above, it is in many cases attractive to subject the resultant demetallized hydrocarbon oil to a hydrodesulphurization treatment and it is advantageous to carry out the demetallization and desulphurization in one continuous treatment without intermediate isolation and/or purification of the demetallized hydrocarbon oil and of the hydrogen-containing gas becoming available from the final reactor bed of demetallization catalyst.

For the hydrodesulphurization of heavy hydrocarbon fractions, such as residual fractions, specific catalysts are known which can be used for a long time without replacement or regeneration of the catalyst being necessary as a result of deposition of coke and high-molecular components (such as resins, polyaromatics and asphaltenes) from the feed. Catalysts as described in the Dutch patent application 7010427 are very suitable. The particles of said catalysts have a pore volume above 0.30 ml/g, of which pore volume less than 10% is present in pores having a diameter above 100 nm, and the catalyst particles have a specific pore diameter expressed in nm from $7.5 \times d^{0.9}$ to $17 \times d^{0.9}$, in which d represents the specific particle diameter in mm.

Said catalysts very suitably contain a carrier on which one or more metals chosen from the group consisting of nickel, cobalt, tungsten and molybdenum, and in particular one metal of the group consisting of nickel and cobalt and one metal of the group consisting of tungsten and molybdenum, are deposited. Catalysts containing nickel or cobalt together with molybdenum are particularly suitable. The metals are preferably present as their oxides or sulphides. Very suitable carriers are silica, silica-alumina and in particular alumina.

The hydrodesulphurization is carried out under the usual conditions. The demetallized

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hydrocarbon oil to be desulphurized together with the hydrogen-containing gas obtained in the demetallization (to which extra hydrogen is added, if desired) is very suitably passed in downward direction over the catalyst at a temperature between 350 and 475°C (preferably between 385 and 445°C), a total pressure between 75 and 250 bar (preferably between 100 and 225 bar), a hydrogen partial pressure between 35 and 120 bar (preferably between 50 and 100 bar), a space velocity of 0.1—25 (preferably 0.2—5) parts by volume of feed per part by volume of catalyst and a hydrogen/feed ratio of 150—2000 (preferably 250—1500) N1 of H₂/kg of feed.

The desulphurization catalyst is very suitably contained in one or more fixed beds which, if desired, are located in several serially connected reactors.

When the demetallization catalyst or the desulphurization catalyst is deactivated, the whole plant is closed down and the demetallization catalyst and desulphurization catalyst are both removed and/or regenerated. For economic reasons the aim will be to choose the quantities of demetallization catalyst and desulphurization catalyst in such a manner that both are deactivated about simultaneously, since in that manner no or only a small portion of active catalyst is removed and/or subjected to a regeneration process. The product obtained after the desulphurization is separated from the hydrogen-containing gas in the usual manner; if desired, said gas can be recycled to the process after complete or partial removal of H₂S and any other impurities.

The invention also relates to an apparatus consisting of one or more serially connected reactors each of which can be filled with one or more fixed catalyst beds, the first bed of the first reactor having an inlet for a gas and an inlet for a hydrocarbon oil, characterized in that at least two inlets for hydrocarbon oil is/are present downstream, and that each hydrocarbon oil inlet can be separately connected or closed.

The invention will now be illustrated with reference to the following diagrammatic figure. Each of the reactors R1, R2 and R3 contains two fixed beds of demetallization catalyst (1, 2, 3, 4, 5 and 6). Hydrogen is supplied to the bed 1 in reactor R1 through a line 7, passes the beds 2, 3, 4, 5 and 6 consecutively and leaves reactor R3 through a line 8 together with demetallized hydrocarbon oil. Fresh hydrocarbon oil is supplied through a line 9 and is initially supplied to bed 1 via an open valve 10 and passes through the beds 1, 2, 3, 4, 5 and 6 consecutively. Valves 11, 12, 13, 14 and 15 are closed. After the demetallization catalyst in bed 1 is deactivated, valve 11 is opened and valve 10 is closed. The hydrocarbon oil to be demetallized is then supplied to bed 2 and passes through the beds 2, 3, 4, 5 and 6 consecutively. When bed 2 is deactivated, valve 12 is opened and valve 11 is closed and the hydro-

carbon oil to be demetallized is supplied to bed 3. In a similar manner the hydrocarbon oil to be demetallized is supplied to the beds 4, 5, 6 whenever the preceding bed is deactivated. After bed 6 is also deactivated, the hydrocarbon oil and hydrogen streams are interrupted and the catalyst in reactors R₁, R₂ and R₃ is replaced or regenerated. In the figure the resultant demetallized hydrocarbon oil and the hydrogen-containing gas which become available through a line 8 from reactor R3 are passed without further purification through the reactors R4 and R5, each containing two beds of a desulphurization catalyst. The desulphurized and demetallized hydrocarbon oil and the hydrogen-containing gas becoming available from reactor R5 through a line 16 can be separated and purified by conventional methods. As regards pressure, temperature and space velocity, conditions suitable for demetallization are maintained in reactors R₁, R₂ and R₃ and conditions suitable for desulphurization are maintained in reactors R4 and R5.

Example

In an apparatus as described in the figure, beds 1—6 in the reactors R1, R2 and R3 are filled with a demetallization catalyst. Said catalyst contains 0.6% by weight of nickel (as oxide) and 1.9% by weight of vanadium (as oxide) on silica as carrier, has a specific average pore diameter of 13.6 nm, a specific average particle diameter of 2.2 mm, a specific surface area of 262 m²/g and a pore volume of 0.78 ml/g, of which pore volume 0.3% consists of pores having a diameter above 100 nm. Before use the catalyst is sulphided by passing over it a gasoil containing 1.6% by weight of sulphur, at a space velocity of 1 kg/litre of catalyst/h, a temperature of 350°C and a hydrogen pressure of 50 bar. The reactors R4 and R5 are filled with a desulphurization catalyst. This catalyst contains 3.6% by weight of nickel (as oxide) and 8.9% by weight of molybdenum (as oxide) on alumina as carrier, and has a specific average pore diameter of 20.2 nm, a specific average particle diameter of 1.5 mm, a specific surface area of 183 m²/g and a pore volume of 0.54 ml/g, of which less than 0.4% is present in pores having a diameter above 100 nm. Before use this desulphurization catalyst is sulphided in the same way as the demetallization catalyst.

A deasphalted vacuum residue of a mineral oil (DAO) containing 40 ppm of vanadium and 2.7% by weight of sulphur, is subsequently passed through the reactors R1—R5 at a space velocity of 0.29 kg/l of catalyst/h both for the demetallization catalyst and the desulphurization catalyst, at a temperature of 390°C, a hydrogen partial pressure of 70 bar and a gas space velocity of 1000 N1/kg of feed. Whenever the pressure drop increases rapidly, the feed inlet is moved to the next bed of demetallization catalyst, the hydrogen stream being main-

tained over all the beds. The test is interrupted after unacceptable pressure drop occurs while the feed is being supplied to bed 6; this is 12,000 hours after the start of the test. The product obtained contains 1 ppm of vanadium and 0.5% by weight of sulphur.

For the sake of comparison an experiment is carried out in which the feed inlet is not moved downstream. After only 2000 hours such a pressure drop occurs that the experiment must be interrupted.

Claims

1. A process for the demetallization of a hydrocarbon oil by passing said oil together with hydrogen over one or more fixed beds of a demetallization catalyst, characterized in that whenever that catalyst portion which is first contacted with the hydrocarbon oil is deactivated, the point of supply of the hydrocarbon oil is removed downstream, at least part of the original supply of hydrogen being maintained over the entire catalyst.

2. A process as claimed in claim 1, characterized in that the demetallization catalyst is contained in several serially connected beds.

3. A process as claimed in claim 2, characterized in that the point of supply of the hydrocarbon oil to be demetallized is moved to a point between an exhausted catalyst bed and the next fresh catalyst bed.

4. A process as claimed in any one of the preceding claims, characterized in that the hydrocarbon oil is a residual fraction.

5. A process as claimed in any one of the preceding claims, characterized in that the demetallization catalyst contains at least one metal of the group consisting of nickel and cobalt, at least one metal of the group consisting of molybdenum, vanadium and tungsten, supported on a carrier, and fulfils the following requirements:

- 1) $p/d > 3.5 - 0.02 v$, where p represents the specific average pore diameter in nm, d represents the specific average particle diameter in mm and v is the percentage of the total pore volume consisting of pores having a diameter above 100 nm,
- 2) the total pore volume is above 0.40 ml/g,
- 3) v is below 50 and
- 4) the specific surface area is above 100 m²/g; in case the catalyst has such a p and d that the quotient p/d is above 3.5—0.02 v , but at most 10—0.15 v , the catalyst must fulfil the following additional requirements:
 - a) the nitrogen pore volume is above 0.60 ml/g,
 - b) the specific surface area is above 150 m²/g and
 - c) p is above 5 nm.

6. A process as claimed in any one of the preceding claims, characterized in that the

demetallization is carried out at a temperature between 350 and 425°C, a total pressure between 100 and 200 bar, a hydrogen partial pressure between 50 and 100 bar, a space velocity of 0.1—25 parts by volume of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 200—1500 NI of H₂/kg of feed.

7. A process as claimed in claim 6, characterized in that the demetallized hydrocarbon oil is subjected to a hydrodesulphurization treatment.

8. A process as claimed in claim 7, characterized in that the demetallization and desulphurization are carried out in one continuous treatment without intermediate isolation and/or purification of the demetallized hydrocarbon oil and of the hydrogen-containing gas becoming available from the final reactor bed of demetallization catalyst.

9. An apparatus consisting of one or more serially connected reactors each of which can be filled with one or more fixed catalyst beds, the first bed of the first reactor having an inlet for a gas and an inlet for a hydrocarbon oil, characterized in that at least two hydrocarbon oil inlets are present downstream and that each hydrocarbon oil inlet can be separately connected or closed.

Revendications

1. Un procédé pour la démétallisation d'une huile d'hydrocarbures en faisant passer cette huile en même temps que de l'hydrogène sur un ou plusieurs lits fixes d'un catalyseur de démétallisation, caractérisé en ce que chaque fois que la portion de catalyseur qui est mise initialement en contact avec l'huile d'hydrocarbures est désactivé, le point d'introduction de l'huile d'hydrocarbures est déplacé vers l'aval, au moins une partie du courant initial d'hydrogène étant maintenue sur le catalyseur entier.

2. Un procédé selon la revendication 1, caractérisé en ce que le catalyseur de démétallisation est contenu dans plusieurs lits disposés en série.

3. Un procédé selon la revendication 2, caractérisé en ce que le point d'introduction de l'huile d'hydrocarbures à démétalliser est amené à un endroit situé entre un lit de catalyseur épuisé et le lit suivant de catalyseur frais.

4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'huile d'hydrocarbures est une fraction résiduelle.

5. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le catalyseur de démétallisation contient au moins un métal du groupe constitué par le nickel et le cobalt, au moins un métal du groupe constitué par le molybdène, le vanadium et le tungstène déposés sur un support, et remplit les conditions suivantes:

tained over all the beds. The test is interrupted after unacceptable pressure drop occurs while the feed is being supplied to bed 6; this is 12,000 hours after the start of the test. The product obtained contains 1 ppm of vanadium and 0.5% by weight of sulphur.

For the sake of comparison an experiment is carried out in which the feed inlet is not moved downstream. After only 2000 hours such a pressure drop occurs that the experiment must be interrupted.

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2. A process as claimed in claim 1, characterized in that the demetallization catalyst is contained in several serially connected beds.

3. A process as claimed in claim 2, characterized in that the point of supply of the hydrocarbon oil to be demetallized is moved to a point between an exhausted catalyst bed and the next fresh catalyst bed.

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- 1) $p/d > 3.5-0.02 v$, where p represents the specific average pore diameter in nm, d represents the specific average particle diameter in mm and v is the percentage of the total pore volume consisting of pores having a diameter above 100 nm,
- 2) the total pore volume is above 0.40 ml/g,
- 3) v is below 50 and
- 4) the specific surface area is above 100 m²/g; in case the catalyst has such a p and d that the quotient p/d is above 3.5—0.02 v , but at most 10—0.15 v , the catalyst must fulfil the following additional requirements:
 - a) the nitrogen pore volume is above 0.60 ml/g,
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6. A process as claimed in any one of the preceding claims, characterized in that the

demetallization is carried out at a temperature between 350 and 425°C, a total pressure between 100 and 200 bar, a hydrogen partial pressure between 50 and 100 bar, a space velocity of 0.1—25 parts by volume of fresh feed per part by volume of catalyst per hour and a hydrogen/feed ratio of 200—1500 NI of H₂/kg of feed.

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4. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'huile d'hydrocarbures est une fraction résiduelle.

5. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le catalyseur de démétallisation contient au moins un métal du groupe constitué par le nickel et le cobalt, au moins un métal du groupe constitué par le molybdène, le vanadium et le tungstène déposés sur un support, et remplit les conditions suivantes:



- 1) $p/d > 3,5-0,02$ v, où p représente le diamètre moyen spécifique des pores en nm, d représente le diamètre moyen spécifique des particules en mm et v est le pourcentage du volume total des pores constitué de pores ayant un diamètre de plus de 100 nm,
- 2) le volume total des pores est supérieur à $0,40 \text{ cm}^3/\text{g}$,
- 3) v est inférieur à 50 et
- 4) la surface spécifique est supérieure à $100 \text{ m}^2/\text{g}$; dans le cas où le catalyseur a un p et un d tels que le quotient p/d soit supérieur à $3,5-0,02$ v, mais est au maximum $10-0,15$ v, le catalyseur doit remplir les conditions supplémentaires suivantes:
 - a) le volume de pores déterminé à l'azote est supérieur à $0,60 \text{ cm}^3/\text{g}$,
 - b) la surface spécifique est supérieure à $150 \text{ m}^2/\text{g}$ et
 - c) p est supérieur à 5 nm.

6. Un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la démétallisation est effectuée à une température comprise entre 350 et 425°C , une pression totale comprise entre 100 et 200 bars, une pression partielle d'hydrogène comprise entre 50 et 100 bars, une vitesse spatiale de $0,1-25$ parties en volume de charge fraîche par partie en volume de catalyseur et par heure et un rapport hydrogène/charge de $200-1500$ litres (TPN) de H_2 par kg de charge.

7. Un procédé selon la revendication 6, caractérisé en ce que l'huile d'hydrocarbures démétallisée est soumise à un traitement d'hydrodésulfuration.

8. Un procédé selon la revendication 7, caractérisé en ce que la démétallisation et la désulfuration sont effectuées en un traitement continu sans isolement et/ou purification intermédiaires de l'huile d'hydrocarbures démétallisée et du gaz contenant de l'hydrogène devenant disponibles à la sortie du lit de réacteur final de catalyseur de démétallisation.

9. Un appareil constitué d'un ou plusieurs réacteurs disposés en série dont chacun peut être rempli d'un ou plusieurs lits fixes de catalyseur, le premier lit du premier réacteur ayant au moins une entrée pour un gaz et une entrée pour une huile d'hydrocarbures, caractérisé en ce qu'au moins deux entrées pour huile d'hydrocarbures sont présentes en aval et que chaque entrée pour huile d'hydrocarbures peut être séparément connectée ou fermée.

Patentansprüche

1. Ein Verfahren zur Entmetallisierung eines Kohlenwasserstofföls durch Überleiten dieses Öls zusammen mit Wasserstoff über ein oder mehrere Festbetten eines Entmetallisierungskatalysators, dadurch gekennzeichnet, daß immer dann, wenn derjenige Katalysatoranteil, der zuerst mit dem Kohlenwasserstoff in Berüh-

rung kommt, deaktiviert ist, die Zusp eisungsstelle des Kohlenwasserstofföls stromabwärts verlegt wird, wobei mindestens ein Teil der ursprünglichen Wasserstoffzufuhr über dem Gesamtkatalysator aufrechterhalten wird.

2. Ein Verfahren wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß der Entmetallisierungskatalysator in mehreren serienmäßig miteinander verbundenen Betten enthalten ist.

3. Ein Verfahren wie in Anspruch 2 beansprucht, dadurch gekennzeichnet, daß die Zusp eisungsstelle für das zu entmetallisierende Kohlenwasserstofföl zu einem Punkt zwischen einem erschöpften Katalysatorbett und dem nächsten frischen Katalysatorbett verlegt wird.

4. ein Verfahren wie in irgendeinem der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß das Kohlenwasserstofföl eine Rückstandsfraction ist.

5. Ein Verfahren wie in irgendeinem der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß der Entmetallisierungskatalysator mindestens ein Metall aus der Gruppe, bestehend aus Nickel und Kobalt, mindestens ein Metall aus der Gruppe, bestehend aus Molybdän, Vanadium und Wolfram, aufgebracht auf einen Träger, enthält und die nachstehenden Bedingungen erfüllt:

- 1) $p/d > 3,5-0,02$ v, wobei p den spezifischen mittleren Porendurchmesser in nm bedeutet, d den spezifischen mittleren Teilchendurchmesser in mm bedeutet und v der Prozentgehalt des gesamten Porenvolumens, welcher aus Poren mit einem Durchmesser oberhalb 100 nm besteht, ist,
- 2) das gesamte Porenvolumen mehr als $0,40 \text{ ml/g}$ beträgt,
- 3) v unterhalb 50 liegt und
- 4) die spezifische Oberfläche oberhalb $100 \text{ m}^2/\text{g}$ liegt; falls der Katalysator solche Werte für p und d aufweist, daß der Quotient p/d oberhalb $3,5-0,02$ v liegt, aber höchstens $10-0,15$ v beträgt, muß der Katalysator die folgenden zusätzlichen Bedingungen erfüllen:
 - a) das mit Stickstoff bestimmte Porenvolumen liegt oberhalb $0,60 \text{ ml/g}$,
 - b) die spezifische Oberfläche liegt oberhalb $150 \text{ m}^2/\text{g}$ und
 - c) p liegt oberhalb 5 nm.

6. Ein Verfahren wie in irgendeinem der vorhergehenden Ansprüche beansprucht, dadurch gekennzeichnet, daß die Entmetallisierung bei einer Temperatur zwischen 350 und 425°C , einem Gesamtdruck zwischen 100 und 200 bar, einem Wasserstoffpartialdruck zwischen 50 und 100 bar, einer Raumgeschwindigkeit von $0,1$ bis 25 Volumenteilen frischer Beschickung je Volumenteil Katalysator je Stunde und einem Verhältnis Wasserstoff/Beschickung von 200 bis $1500 \text{ Nl Wasserstoff/kg Beschickung}$ durchgeführt wird.



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7. Ein Verfahren wie in Anspruch 6 beansprucht, dadurch gekennzeichnet, daß das entmetallisierte Kohlenwasserstofföl einer Hydroentschwefelungsbehandlung unterworfen wird.

8. Ein Verfahren wie in Anspruch 7 beansprucht, dadurch gekennzeichnet, daß die Entmetallisierung und die Entschwefelung in einer einzigen kontinuierlichen Behandlung ohne Zwischenisolierung und/oder Reinigung des entmetallisierten Kohlenwasserstofföls und des wasserstoffhaltigen Gases durchgeführt wird, welches aus dem letzten Reaktorbett des Entmetallisierungskatalysators erhältlich ist.

9. Eine Vorrichtung, bestehend aus einem oder mehreren serienmäßig miteinander verbundenen Reaktoren, von denen jeder mit einem oder mehreren festen Katalysatorbetten angefüllt werden kann, wobei das erste Bett des ersten Reaktors einen Einlaß für ein Gas und einen Einlaß für ein Kohlenwasserstofföl aufweist, dadurch gekennzeichnet, daß mindestens 2 Kohlenwasserstofföleinlässe stromabwärts gelegen vorhanden sind, und daß jeder Kohlenwasserstofföleinlaß getrennt zugeschaltet oder abgeschaltet werden kann.

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