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**Process for the catalytic hydrodesulphurization of a residual fraction of a hydrocarbon oil.**

A process for the catalytic hydrodesulphurization of a residual fraction of a hydrocarbon oil (1) with a high metal content by passing a blend of part of said residual fraction (1) and at least part of a distillate fraction of a hydrocarbon oil (3) with a lower metal content over a catalyst (5) in the presence of hydrogen, (4) and supplying the remainder of the residual fraction (9) to the catalyst at one or more downstream points (8,10,11).

**EP 0 021 495 A1**

PROCESS FOR THE CATALYTIC HYDRODESULPHURIZATION  
OF A RESIDUAL FRACTION OF A HYDROCARBON OIL

The invention relates to a process for the catalytic hydrodesulphurization of a residual fraction of a hydrocarbon oil with a high metal content.

When refining hydrocarbon oils, such as mineral  
5 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 (the short residue) is deasphalted,  
10 in which process deasphalted vacuum residue of a mineral oil (referred to as DAO below) and asphalt are obtained. The heavier fractions obtained in the vacuum distillation (also known as vacuum distillate fractions) and the residual fractions, in particular DAO,  
15 can be used inter alia as heavy fuel or as feedstock for catalytic cracking. In order to discharge the smallest possible quantity of sulphur compounds to the atmosphere in the combustion of heavy fuel, it is necessary that the sulphur content of oils to be used  
20 as heavy fuel is as low as possible. If DAO and/or vacuum distillate fractions are used as feed for a catalytic cracking reaction the metal content and the tendency toward coke deposition of the feed to be used must be as low as possible in order to prevent rapid  
25 deactivation of the cracking catalyst.

In order to meet the requirements laid down regarding sulphur and metal content, both vacuum distillate fractions and residual fractions (by which are meant fractions which have remained behind as  
30 residue in vacuum distillation or have been obtained from such residue, for example short residue, DAO, asphalt) must generally be desulphurized, and at least part of the metals, which occur in a larger quantity

in the residual fractions than in the vacuum distillate fractions, must be removed. These metals consist for the greater part of nickel and vanadium, which may be present in substantial quantities in hydrocarbon oils, such as mineral oils.

In this application, by a "high metal content" is meant a metal content which is so high that the usual catalysts for hydrodesulphurization are not resistant thereto.

The catalysts usually used for catalytic desulphurization are not resistant to quantities of metal in the feed which are higher than about 20 parts by weight per million (ppm), since in the case of larger quantities of metal an unacceptable pressure drop across the catalyst occurs after a relatively short time. For this reason a residual fraction, for example DAO, having a metal content which is substantially higher than 20 ppm cannot be desulphurized by means of these catalysts in an economically justified manner.

The metal content of the residual fraction can be so high that even after blending the whole quantity of residual fraction to be desulphurized with available vacuum distillate fractions (the latter fractions containing only small quantities of metal) the metal content of the blend is still too high for desulphurization by means of the usual catalysts. It is of course possible to demetallize the residual fraction before desulphurization by means of a suitable catalyst, but this requires the construction and operation of extra plants, which is unattractive in many cases.

The invention provides a process by which, with the application of catalytic hydrodesulphurization only and without the life of the desulphurization catalyst being reduced unacceptably, it is still



possible to obtain products having desired low sulphur and low metal contents.

The invention therefore relates to a process for the catalytic hydrodesulphurization of a residual fraction of a hydrocarbon oil with a high metal content, characterized in that a blend of part of said residual fraction and at least part of a distillate fraction of a hydrocarbon oil with a lower metal content is passed over a catalyst in the presence of hydrogen, and the remainder of the residual fraction is supplied to the catalyst at one or more downstream points.

As hydrocarbon oils may be mentioned mineral oils, such as shale oil, oil recovered from tar sands, and in particular petroleum.

As distillate fraction of a hydrocarbon oil, such as of a mineral oil, use is very suitably made of a vacuum distillate fraction, in particular a "flashed distillate", that is a high-boiling oil which is obtained from petroleum by vacuum flash distillation. The boiling range of a flashed distillate generally lies, entirely or largely, between 300 and 550°C, and the metal content is generally less than 5 ppm, in particular less than 2 ppm.

As a residual fraction a deasphalted vacuum residue (DAO) is very suitably used; the metal content thereof is generally considerably higher, for example, 20-60 ppm.

By blending at least part of the distillate fraction with part of the residual fraction a blend can be obtained which has a much lower metal content than the residual fraction. For said blend use is preferably made of all the flashed distillate becoming available in the vacuum distillation for the preparation of the relevant residual fraction, such a quantity of residual fraction being incorporated into

the blend that the metal content thereof is so low that the blend can be hydrodesulphurized without objection by means of a usual desulphurization catalyst. The quantities of metal which the blend may  
5 contain are of course dependent on the "metal sensitivity" (an indication of the quantity of metal which may still be present in the feed without giving rise to problems) of the specific desulphurization catalyst one intends to use. Use is preferably made of a de-  
10 sulphurization catalyst which with the application of feeds containing up to 20 ppm of metal is still satisfactory in operation.

The remainder of the residual fraction is supplied at one or more points downstream of the cata-  
15 lyst. Since said points of the catalyst are also passed by the blend which has been supplied as feed at the beginning of the process and which is already completely or partly desulphurized and demetallized, the residual fraction is blended therewith and the  
20 blend thus obtained again has a metal content which is not detrimental to the desulphurization catalyst. If the residual fraction has a very high metal content and the metal content of the blend obtained during the addition of the entire remainder of the residual  
25 fraction were to become too high at one downstream point, the remainder of the residual fraction is supplied to the catalyst in various portions, each portion further downstream than the previous one.

If desired, part of the distillate fraction can  
30 also be supplied at one or more downstream points. Very suitably various catalyst beds are used in series. They are preferably arranged in several reactors.

It is possible to use as catalyst hydrodesulphu-  
35 rization catalysts known as such, such as catalysts

consisting of a carrier on which one or more metals of groups VIB and VIII of the periodic system (and/or compounds of said metals such as sulphides or oxides thereof) have been deposited. Catalysts which contain cobalt and/or nickel together with molybdenum and/or tungsten are very suitable. Silica, alumina and silica-alumina are very suitable as carriers. Preference is given to catalysts containing 2-6% by weight of nickel (calculated as oxide) and 8-16% by weight of molybdenum calculated as oxide (percentages based on carrier) on an alumina carrier having a surface area of 100-300 m<sup>2</sup>/g and a pore volume of 0.3-0.7 ml/g, since catalysts of this type have a relatively low metal sensitivity, that is to say that feeds with a relatively high metal content (up to about 20 ppm) can be used without the occurrence of undesirable effects. The catalysts are preferably sulphided before use.

The reaction conditions during the hydrodesulphurization are the usual ones. Suitable are temperatures of 300-450°C, a total pressure of 45-150 bar, a hydrogen partial pressure of 30-120 bar, a space velocity of 0.1-8.0 kg of feed per kg of catalyst per hour and a quantity of hydrogen of 250-2000 nl per litre of feed. Very suitable are temperatures of 330-390°C, a total pressure of 70-95 bar, a hydrogen partial pressure of 50-80 bar, a space velocity of 0.2-0.4 kg of feed per kg of catalyst per hour, and a quantity of hydrogen of 400-900 nl per litre of feed.

The oil to be desulphurized and hydrogen may be passed countercurrently over the catalyst, but it is preferred to pass the oil to be desulphurized and the hydrogen over the catalyst in the same, preferably downward, direction, in which case the hydrogen can be completely or partly dissolved in the oil.

The invention will now be illustrated with refer-

ence to the Figure. This Figure is diagrammatical and auxiliaries which are immaterial to the nature of the invention, such as pumps, valves, heat exchangers and furnaces, have been omitted.

5       Through a line 1 residual fraction is supplied, part of which is blended through a line 2 with distillate fraction supplied through a line 3. To the blend thus obtained hydrogen is supplied through a line 4 and the blend of oil and hydrogen is supplied  
10       to a reactor 6 through a line 5. This reactor is filled with one or more fixed catalyst beds. Under the conditions prevailing in said reactor the oil blend introduced is desulphurized and subsequently supplied to a reactor 8 through a line 7. The remainder of the  
15       residual fraction is supplied to the line 7 through a line 9. In the reactor 8 and the reactors 10 and 11 (each reactor contains one or more catalyst beds) connected thereafter, the oil is desulphurized further and the product is discharged through a line 12.

20       The resultant product can be separated into gas and liquid in the known manner and, if desired, the resultant desulphurized liquid can be separated by distillation into desulphurized residual fraction and desulphurized distillate fraction.

25       EXAMPLE I

      To 100 parts of flashed distillate with a sulphur content of 2.3% by weight and a metal content of 2 parts by weight per million (ppm), 36 parts of DAO having a sulphur content of 2.7% by weight and a metal  
30       content of 40 ppm are added. The resultant blend has a metal content of 12.1 ppm and a sulphur content of 2.4% by weight. The blend is passed downwards over a catalyst in a first reactor in the presence of hydrogen, in which step the metal content of the blend is  
35       reduced to <1 ppm.

The catalyst consisted of an alumina carrier with a surface area of  $246 \text{ m}^2/\text{g}$  and a pore volume of  $0.6 \text{ ml/g}$ , on which 3.7% by weight of nickel oxide and 13.2% by weight of molybdenum oxide (percentages based on carrier) had been deposited. The catalyst had been sulphided before use.

To the 136 parts of demetallized stream a further 54 parts of the above-mentioned DAO are subsequently added, with the result that the metal content of the blend is again brought to 12.1 ppm. This blend is passed to a second reactor with identical desulphurization catalyst and desulphurized therein to a final sulphur content of 0.45% by weight. In order to maintain the sulphur content at said level the reactor temperatures are gradually increased during the test. At the same time the metal content falls to  $<1 \text{ ppm}$ . The conditions are summarized in the following table.

#### Conditions

Space velocity	0.32 kg/l/h
Hydrogen partial pressure (oulet 2nd reactor)	70 bar
Average reactor temperature at start of test	$330^\circ\text{C}$
Average reactor temperature at end of test	$370^\circ\text{C}$
Hydrogen/feed ratio	650 nl/l.

By maintaining the above-mentioned method of operation a catalyst life of 12,000 hours is obtained; subsequently a rapid deactivation of the catalyst occurs.

#### EXAMPLE II

In a comparative test the same quantity of sulphur as in Example I, i.e.  $\Delta S_{\text{feed-product}}$  equalling 1.95% by weight of S, is removed from 190 parts of DAO (identical with that of Example I, metal content 40 ppm, sulphur content 2.7% by weight), now without dilution with flashed distillate and without downstream addition of DAO. Use is made of a desulphur-



ization catalyst identical to that described in Example I.

Conditions

	Space velocity	0.80 kg/l/h
5	Hydrogen partial pressure (outlet reactor)	70 bar
	Average reactor temperature at start of test	330°C
	Average reactor temperature at end of test	370°C
	Hydrogen/feed ratio	650 nl/l

As a consequence of the high metal content of the DAO the catalyst life is now drastically limited to 1750 hours, or about 15% of the life obtained in Example I. Subsequently a rapid deactivation of the catalyst occurs.

EXAMPLE III

15 In a comparative test 100 parts of flashed distillate and 90 parts of DAO (both identical with that used in Example I) are completely intermixed and passed as such over a desulphurization catalyst (identical with that described in Example I). The sulphur content and metal content of this mixture were 2.5% by weight and 20 ppm respectively. The same quantity of sulphur is removed as in Example I) ( $\Delta S_{\text{feed-product}}$  1.95% by weight).

Conditions

25	Space velocity	0.54 kg/l/h
	Hydrogen partial pressure (outlet reactor)	70 bar
	Average reactor temperature at start of test	330°C
	Average reactor temperature at end of test	370°C
	Hydrogen/feed ratio	650 nl/l

30 The life of the desulphurization catalyst is now 5,900 hours, 49% of that obtained in Example I. Subsequently a rapid deactivation of the catalyst occurs.

EXAMPLE IV

35 In a comparative test 100 parts of flashed distillate and 90 parts of DAO (both identical with that

used in Example I) are completely intermixed and passed as such over a Ni/Mo desulphurization catalyst (identical with that of Example I). The S-content and the metal content of this mixture were 2.5% by weight and 20 ppm respectively.

The same space velocity as in Example I is used. The metal content of the product is reduced to <1 ppm. The removed quantity of sulphur ( $\Delta S_{\text{feed-product}}$ ) is 2.3% by weight.

10 Conditions

Space velocity	0,32 kg/l/h
Hydrogen partial pressure (outlet reactor)	70 bar
Average reactor temperature at start of test	330°C
Average reactor temperature at end of test	370°C
15 Hydrogen/feed ratio	650 nl/l

The life of the desulphurization catalyst is now 4,100 hours, 34% of that of Example I. Subsequently a rapid deactivation of the catalyst occurs.

C L A I M S

1. A process for the catalytic hydrodesulphurization of a residual fraction of a hydrocarbon oil with a high metal content, characterized in that a blend of part of said residual fraction and at least part of a distillate fraction of a hydrocarbon oil with a lower metal content, is passed over a catalyst in the presence of hydrogen, and the remainder of the residual fraction is supplied to the catalyst at one or more downstream points.
2. A process as claimed in claim 1, characterized in that the hydrocarbon oil is a mineral oil.
3. A process as claimed in claims 1-2, characterized in that the residual fraction is a deasphalted vacuum residue of a mineral oil.
4. A process as claimed in any one of the preceding claims, characterized in that the distillate fraction of a hydrocarbon oil is a vacuum distillate fraction.
5. A process as claimed in claim 4, characterized in that the vacuum distillate fraction is a flashed distillate.
6. A process as claimed in claim 5, characterized in that all the flashed distillate becoming available in the vacuum distillation for the preparation of the relevant residual fraction is incorporated into the blend with part of the residual fraction.
7. A process as claimed in any one of the preceding claims, characterized in that the catalyst contains cobalt and/or nickel together with molybdenum and/or tungsten (and/or compounds of these metals) on a carrier.
8. A process as claimed in claim 7, characterized in that the catalyst contains 2-6% by weight of nickel (calculated as oxide) and 8-16% by weight of molybdenum (calculated as oxide) on an alumina carrier



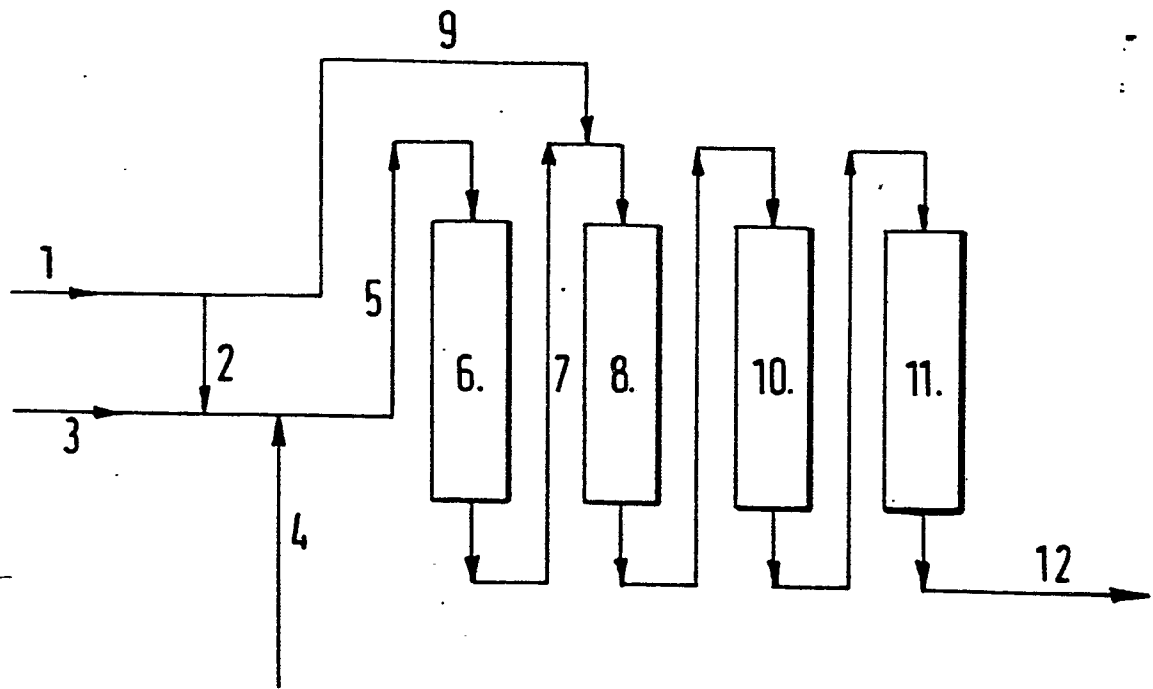
having a surface area of 100-300 m<sup>2</sup>/g and a pore volume of 0.3-0.7 ml/g.

9. A process as claimed in any one of the preceding claims, characterized in that the oil to be desulphurized and the hydrogen are passed over the catalyst in the same direction.

10. A process as claimed in any one of the preceding claims, characterized in that the hydrodesulphurization is carried out at a temperature of 300-450°C, a total pressure of 45-150 bar, a hydrogen partial pressure of 30-120 bar, a space velocity of 0.1-8.0 kg of feed per kg of catalyst per hour and a quantity of hydrogen of 250-2000 nl per litre of feed.

11. A process as claimed in claim 10, characterized in that the hydrodesulphurization is carried out at a temperature of 330-390°C, a total pressure of 70-95 bar, a hydrogen partial pressure of 50-80 bar, a space velocity of 0.2-0.4 kg of feed per kg of catalyst per hour and a quantity of hydrogen of 400-900 nl per litre of feed.

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European Patent  
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# EUROPEAN SEARCH REPORT

0021495

Application number

EP 80 20 0531

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 4 016 069</u> (R.D. CHRISTMAN) * Abstract; column 1, lines 6-45; column 1, line 55 - column 2, line 30; column 5, lines 15- 36; column 6, line 45 - column 7, line 18; claims 1-8; figure 4 *	1,2,7- 11	C 10 G 65/00 45/02
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	<u>DE - A - 2 730 698</u> (EXXON) * Claims 1-38; page 17; pages 13, 14; example 1; tables 3,4 *	1,2,3, 7-11	TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
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	<u>FR - A - 2 232 587</u> (BASF) * Page 1, lines 1-9; page 4, lines 3-30; page 5, lines 1-31; claims 1-5 *	1,2,9	C 10 G 45/00 45/02 65/00 65/02 65/04 65/14 65/16
	<u>US - A - 3 830 728</u> (W. MOUNCE) * Abstract; column 1, line 50 - column 2, line 7; column 2, lines 52-72; column 3, lines 13-55; claims 1-5 *	1,7,10, 11	
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	<u>US - A - 3 420 768</u> (B.G. BRAY)		CATEGORY OF CITED DOCUMENTS
	----		X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 30-09-1980	Examiner LO CONTE