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HYDROCRACKING PROCESS

The present invention relates to an improved petroleum hydrocracking process.

There are a large number of processes for hydrocracking petroleum hydrocarbon feedstocks and numerous catalysts that are used in these processes. Many of these processes comprise two stages, a feed preparation stage and a hydrocracking stage, the two stages operating with different catalysts. The first stage, in general, contains a hydrodenitrogenation/hydrodesulphurization catalyst which also may include a hydrocracking function for mild hydrocracking and the second stage contains a hydrocracking catalyst. Product from the first stage may be treated to remove ammonia and hydrogen sulphide gases prior to being passed to the second stage, or product may be passed directly to the second stage. In this two stage operation, the hydrocracking stage is frequently referred to as a second stage hydrocracker.

Multiple beds in a hydrocracker have been disclosed in U.S. patents 4,797,195; 4,797,196 and 4,834,865.

Hydrocracking catalysts generally comprise a hydrogenation component on an acidic cracking support. More specifically, hydrocracking catalysts comprise one or more hydrogenation components selected from the group consisting of Group VIB metals and Group VIII metals of the Periodic Table of the Elements. Suitably the hydrogenation component(s) is (are) in oxidic and/or sulphided form. The prior art has also taught that these hydrocracking catalysts preferably contain an acidic support comprising a large pore crystalline molecular sieve, particularly an aluminosilicate. These molecular sieves are generally suspended in a refractory inorganic oxide binder such as silica, alumina, or silica-alumina. The oxides such as silica, silica-alumina and alumina have also been used alone as the support for the hydrogenating metals for certain specific operations.

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Regarding the hydrogenation component, the especially preferred Group VIB metals are tungsten and molybdenum and the especially preferred Group VIII metals are nickel and cobalt. The prior art has also taught that combinations of metals for the hydrogenation component in the order of preference are: Ni-W, Ni-Mo, Co-Mo and Co-W. Other hydrogenation components broadly taught by the prior art include iron, ruthenium, rhodium, palladium, osmium, iridium and platinum. Among these latter components, platinum and/or palladium are particularly preferred with palladium being most preferred.

Hydrocracking is a general term which is applied to petroleum refining processes wherein hydrocarbonaceous feedstocks which have relatively high molecular weights are converted to lower molecular weight hydrocarbons at elevated temperature and pressure in the presence of a hydrocracking catalyst and a hydrogen-containing gas. Hydrogen is consumed in the cracking of the high molecular weight compounds to lower molecular weight compounds. Hydrogen will also be consumed in the conversion of any organic nitrogen and sulphur compound to ammonia and hydrogen sulphide as well as in the saturation of olefins and other unsaturated compounds. The hydrocracking reaction is exothermic and when substantially adiabatic reactors are used, as is usually the case, the temperature in the catalyst bed will rise progressively from the beginning to the end of the reactor. Excessive temperature in the reactor can present several problems. High temperatures can damage the catalyst, can result in the safe operating temperature of the reactor being exceeded or can cause the hydrocracking reaction to "run away", with disastrous results. This temperature rise problem can be solved by dividing the catalyst in the reactor into a series of beds with interstage cooling supplied between the beds by the injection of a cooled hydrogen-containing gas stream.

When a multiple bed configuration is used in a second stage hydrocracker, optimum use of the catalyst requires that each bed does a proportionate amount of the hydroconversion. For example in the commonly applied five bed second stage hydrocracker each bed

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should carry out about twenty percent of the hydroconversion, resulting in a temperature rise in each of the beds of about the same degree. It has now been found, however, that in many cases the catalyst in one or more of the first beds is somehow inhibited such that its activity is less than that of the catalyst in the remaining beds. As a result, the first bed carries out less than its proportionate share of hydroconversion, thus resulting in a smaller temperature rise in the first bed than occurs in the remaining beds. Raising the temperature of the feed to the first bed can increase conversion, but can also require excessive cooling between the first and second bed which will result in an inefficient utilization of hydrogen. Further, if the physical configuration of the reactor limits the amount of hydrogen that can be injected between the beds or limits the temperature to which the top bed can be heated, then the top bed can not be operated at its full hydroconversion potential. It has now been found that by modifying the catalyst in one or more of the first beds over that in the remaining beds by providing it with higher hydrogenation metals content and smaller particle size, the conversion in the first bed(s) can be raised to the level in the remaining beds, resulting in a more efficient operation.

Accordingly, the present invention relates to a process for hydrocracking a hydrocarbonaceous feedstock having components boiling above 190 °C comprising reacting the feedstock in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions in a reactor which comprises at least two separate beds of catalyst stacked on top of each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective

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particle diameter of the catalyst used in one or more of the top beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.

5 The term "one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor" refers to the top bed and optionally the next bed or beds in series, without skipping, up to the point wherein the beds contain up to but not exceeding fifty percent by volume of the catalyst used in the reactor. For example, in a six bed reactor with catalyst
10 equally disposed throughout the beds, "one or more of the top beds" will include (a) the top bed, (b) the top bed plus the second (from the top) bed and (c) the top bed plus the second bed plus the third (from the top) bed, but will not include the first bed and third bed (skipping the second bed). The top beds will thus be in
15 contiguous series. The catalyst arranged in the aforementioned top beds will be referred hereinafter as the "top bed catalyst". The catalyst arranged in the remaining beds will be referred hereinafter as the "bottom bed catalyst". Suitably, the reactor has six or five beds. Preferably, the "one or more of the top beds"
20 comprise the top bed and the bed next from the top bed. In another embodiment the "one or more of the top beds" include only the top bed.

The feedstock for the process comprises a heavy oil fraction having a major proportion, say, greater than fifty percent, of its
25 components boiling above 190 °C, preferably above 220 °C or higher. Suitable feedstocks of this type include gas oils such as atmospheric and vacuum gas oils and coker gas oil, visbreaker oil, deasphalted oil, catalytic or thermal cracker cycle oils, synthetic gas oils, coker products and coal liquids. Normally the feedstock
30 will have an extended boiling range, e.g., up to 590 °C or higher, but may be of more limited ranges with certain feedstocks. In general terms, the feedstocks will have a boiling range between about 150 °C and about 650 °C. Typically the feedstock has firstly been subjected to a hydroprocessing step prior to hydrocracking to
35 remove nitrogen, sulphur and heavy metal impurities. This

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hydroprocessing step may also provide some degree of hydrocracking. The hydroprocessed feedstock may be passed directly to the hydrocracker, or it may be processed to remove ammonia, hydrogen sulphide and possibly lower boiling fractions prior to being passed to the hydrocracker.

Operating conditions to be used in the hydrocracking reaction zone include an average catalyst bed temperature within the range of 200 °C to 550 °C, preferably 260 °C to 480 °C, and most preferably 290 °C to 430 °C, a liquid hourly space velocity (LHSV) of 0.1 to 10 volumes of liquid hydrocarbon per hour per volume of catalyst, preferably a LHSV of 0.5 to 5, and a total pressure within the range of 35 to 350 bar, a hydrogen partial pressure within the range of 35 and 310 bar, and a gas/feed ratio between 100 and 5000 Nl/kg feed.

The second stage hydrocracking reactor comprises a vertical reactor having from two to 6 beds of catalyst. Between the beds are placed means for injecting a hydrogen-containing stream into the reactor. This hydrogen-containing stream is cooler than the reactor, say, by 35 °C or more, and serves to cool the process stream as it passes from one bed to the one below. The hydrogen-containing stream may be pure hydrogen or may be admixed with other gases. Typically it is derived from hydrogen-rich processing streams such as those from hydrocarbon dehydrogenation reactors such as catalytic reformers or may be produced via steam-methane reforming. The hydrogen-containing stream is provided to each of the beds in amounts sufficient to maintain an excess of hydrogen throughout the reactor. The hydrocarbonaceous feedstock is heated to reactor temperature prior to being fed to the top bed. Typically, a hydrogen-containing stream is mixed with the feedstock and the mixture is heated to reaction temperature, although the hydrogen-containing stream may be fed separately to the top bed.

The catalysts used in the second stage hydrocracker may comprise metals, oxides and/or sulphides of Group VIB and/or Group VIII elements of the Periodic Table supported on a porous support

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having hydrocracking activity. The key aspect of the present invention is that the top bed catalyst will have a metals content higher and an effective diameter lower than that of the catalyst used in the remaining beds. The metals content of at least one of the hydrogenation components of the top bed catalyst will be 1.5, preferably 2 times the metals content of the corresponding hydrogenation components of the catalyst in the remaining beds when considered as the metal in terms of gram atoms per gram of total catalyst. Suitably the metals content of at least one of the hydrogenation components of the top bed catalyst will be 1.5 to 3, preferably from 1.5 to 2.5 times the metals content of the corresponding hydrogenation components of the catalyst in the remaining beds when considered as the metal in terms of gram atoms per gram of total catalyst. While reference is made herein to the "metals content" of the catalyst, it is understood that this is for measurement reference purposes and that the metal can be in other forms such as the oxide or sulphide. The gram atom per gram of total catalyst is determined by measuring the weight of metal in a gram of catalyst and dividing by the atomic weight of the metal. It is preferred that the catalysts in the beds other than the top bed, i.e., "the remaining beds", be substantially the same. However, it is contemplated that the remaining beds may individually contain catalysts that differ in metals content and average effective diameter, in which case reference to the metals content and average effective diameter of the catalyst in the remaining beds will refer to the maximum metals content and maximum average effective diameter of the catalysts used in the remaining beds.

In general when reference is made herein to the metals content of one or more hydrogenating components selected from Group VIB and Group VIII in the top bed(s) being greater than the content in the remaining bed(s), it is meant that the component in both the top and remaining or bottom beds will be the same component, that is, if the component is platinum in the bottom beds, then platinum will be in the top bed(s) in an increased amount. However, those with

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skill in the hydrocracking art will recognize that certain metals in Group VIB and Group VIII can be interchanged to provide comparable results. It is recognized in Group VIB that molybdenum and tungsten can be interchanged and in Group VIII that nickel and cobalt can be interchanged with each other and platinum and palladium can be interchanged with each other if their respective atomic weights are factored in. Thus, the instant specification and accompanying claims, as appropriate, recognize this equivalency and include the partial or complete substitution of molybdenum for tungsten (and vice versa), cobalt for nickel (and vice versa) and platinum for palladium (and vice versa) in the catalysts used in the top and bottom bed(s).

The average effective particle diameter of the top bed catalyst particles will be at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds. Suitably, the average effective particle diameter of the top bed catalyst particles will be 0.25 to 0.75 times the average effective particle diameter of the catalyst particles used in the remaining beds. Preferably, the particle shapes used in accordance with the present invention will be either cylinders or polylobes or both. The polylobed particles will have from two to five lobes. Trilobes are preferred for use in the top bed. The effective diameter of a particle is defined as the diameter of a sphere with the same surface to volume ratio (S/V) as the particle and can be calculated as 6 times V/S . Average effective particle diameters of catalyst used in the remaining beds will generally range from 0.13 to 0.51 cm. Cylinders are preferably used in the remaining beds.

The active metals component, "the hydrogenation component", of the hydrocracking catalyst is selected from a Group VIB and/or a Group VIII metal component. From Group VIB molybdenum, tungsten and mixtures thereof are preferred. From Group VIII there are two preferred classes: 1) cobalt, nickel and mixtures thereof and 2) platinum, palladium and mixtures thereof. Preferably both Group VIB and Group VIII metals are present. In a particularly preferred embodiment the hydrogenation component is nickel and/or cobalt

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combined with tungsten and/or molybdenum with nickel/tungsten being particularly preferred. The components are suitably present in the oxidic and/or sulphided form. In general the amounts of Group VIB and Group VIII metals present in the catalyst in the beds other than the top bed (the remaining beds) are set out below on an elemental basis and based on the total catalyst weight.

	<u>Suitably</u>	<u>Preferred</u>	<u>Most Preferred</u>
Group VIB	1-30	1-20	2-15
Group VIII	0.05-10	0.1-5	0.2-3.5
Nickel	1-10	1-5	1.5-3.5
Cobalt	1-6	1-5	1.5-4
Tungsten	1-30	2-20	4-15
Molybdenum	1-20	1-15	2-10
Platinum	0.05-5	0.1-2	0.2-1
Palladium	0.05-5	0.1-2	0.2-1

Suitably, the hydrogenation component of the catalyst in the remaining beds comprises between 1 and 10% by weight of nickel and between 1 and 30% by weight of tungsten based on the total catalyst weight. The Group VIB and Group VIII metals are supported on a carrier having hydrocracking activity. Two main classes of carriers known in the art typically include: (a) the porous inorganic oxide carriers selected from alumina, silica, alumina-silica and mixtures thereof and (b) the large pore molecular sieves. Mixtures of the inorganic oxide carriers and the molecular sieves can also be used. The term "silica-alumina" refers to non-zeolitic aluminosilicates.

Suitable supports are the large pore molecular sieves admixed with an inorganic oxide binder, preferably selected from the group consisting of alumina, silica, silica-alumina and mixtures thereof. The molecular sieves have pores greater than 6 Å, preferably between 6 to 12 Å. Suitable wide pore molecular sieves are described in the book Zeolite Molecular Sieves by Donald W. Breck, Robert E. Krieger Publishing Co., Malabar, Fla., 1984. Suitable wide pore molecular sieves comprise the crystalline aluminosilicates.



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silicates, the crystalline aluminophosphates, the crystalline silicoaluminophosphates and the crystalline borosilicates. Preferred are the crystalline aluminosilicates or zeolites. The zeolites are preferably selected from the group consisting of

5 faujasite-type and mordenite-type zeolites. Suitable examples of the faujasite-type zeolites include zeolite Y and zeolite X. Other large pore zeolites such as zeolites L, beta and omega can also be used alone or in combination with the more preferred zeolites.

10 The most preferred support comprises a zeolite Y, preferably an ultrastable zeolite Y (zeolite USY). The ultrastable zeolites used herein are well known to those skilled in the art. They are for instance exemplified in U.S. Pat. Nos. 3,293,192 and 3,449,070. They are generally prepared from sodium zeolite Y by using one or more ammonium ion exchanges followed by steam calcination. They

15 can further be subjected to a so-called dealumination technique to reduce the amount of alumina present in the system. Dealumination techniques are described extensively in the art and comprise inter alia the use of acid extraction, the use of silicon halides or other suitable chemical treating agents, chelates as well as the

20 use of chlorine or chlorine-containing gases at high temperatures. They suitably have low sodium contents of less than 1 percent by weight and a unit cell size of 24.20 to 24.60 Å.

The zeolite is composited with an binder selected from alumina, silica, silica-alumina and mixtures thereof. Preferably

25 the binder is an alumina binder, more preferably a gamma alumina binder or a precursor thereto, such as an alumina hydrogel, aluminum trihydroxide or aluminum oxyhydroxide.

Two classes of zeolite-containing supports are suitably used: (a) those containing a small amount of zeolite and a large amount

30 of "binder", that is, alumina, silica, silica-alumina and mixtures thereof and (b) large amounts of zeolite and small amounts of binder.

The low zeolite-containing support will contain from 1 to 50, preferably from 1 to 25, and more preferably from 1 to 10 percent

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by weight of molecular sieve on a calcined (dehydrated) basis of molecular sieve plus binder with the balance being composed of binder.

5 The high zeolite-containing support suitably contains from 50 to 99, preferably from 60 to 95, and more preferably from 70 to 90 percent by weight of molecular sieve on a calcined (dehydrated) basis of molecular sieve plus binder with the balance being composed of binder.

10 The catalysts can be prepared by traditional methods. For example, the molecular sieve and binder in the form of a hydrogel or hydrosol may be mulled together with water and an optional peptizing agent, formed into extrudates and calcined. The calcined extrudates can be impregnated with one or more solutions containing solubilized salts of Group VIB and Group VIII elements.

15 Alternatively, the hydrogenating components may be mulled into the zeolite/ alumina mixture prior to calcining. Impregnation and mulling may be combined as method for incorporating the hydrogenating components.

The catalysts are normally presulphided prior to use.

20 Typically, the catalysts are presulphided by heating in hydrogen sulphide/hydrogen atmosphere (e.g., 5%v H₂S/95%v H₂) at elevated temperatures, say 370 °C for several hours, e.g. 1-4 hours. Other methods are also suitable for presulphiding and generally comprise heating the catalysts to elevated temperatures (e.g., 204-398 °C)

25 in the presence of hydrogen and sulphur or a sulphur-containing material.

The ranges and limitations provided in the present specification and claims are those which are believed to particularly point out and distinctly define the present invention.

30 It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same way to obtain the same or substantially the same result are intended to be within the scope of the present invention as defined by the present specification and claims.

35 The present invention will now be described by the following examples.

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EXAMPLES

In a commercial second stage hydrocracker having five beds of nickel-tungsten/zeolite USY-alumina catalyst in the shape of 0.32 cm cylinders it was found that the catalyst in the first or top bed was 8-10 °C less active than the catalyst in the lower beds. The reactor normally operates at a LHSV of 1.2 hour⁻¹ to provide a conversion of the feed boiling above 190 °C of 60%. The conversion is calculated from the formula:

$$[\%190\text{ }^{\circ}\text{C}^+(\text{feed}) - \%190\text{ }^{\circ}\text{C}^+(\text{product})] \times 100 / \%190\text{ }^{\circ}\text{C}^+(\text{feed})$$

To model the second stage hydrocracker, a laboratory system was set up. This comprised a 1.9 cm I.D. reactor with a 0.64 cm thermowell running through the centre of the entire length of the 24.1 cm catalyst bed. To prepare the reactor, 20 cm³ of catalyst were diluted with 63 grams of 60x80 mesh silicon carbide and loaded into the reactor in four equally sized aliquots.

Catalyst was presulphided in the laboratory reactor by a programmed heating to 370 °C in 5%v/95%v H₂S/H₂ gas mixture flowing at 100 l/hr.

To model the full length hydrocracker (full bed), feed was provided to the reactor at a LHSV of 1.2 and the temperature was adjusted to provide a conversion of 60%. To model only the top bed of a five bed reactor, feed was provided to the reactor at a LHSV of 6 and the temperature was adjusted to give a conversion of 1/5 of the conversion in the full length reactor or 12%. The temperature of the reactor is a measure of the activity of the catalyst. The more active catalyst can be operated at a lower temperature than a less active catalyst while providing the same conversion.

The laboratory reactor conditions were:

Reactor inlet pressure	103.4 bar
LHSV	1.2* or 6.0** hr ⁻¹
hydrogen/oil ratio	1222 NL/kg
Conversion of 190 °C ⁺	60%* or 12%**
(*for full bed modeling; **for top bed modeling)	

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The feed used was a typical second stage hydrocracker feed fed to a commercial unit, containing recycle and was obtained while the hydrocracker was in the turbine fuel mode of operation. The corresponding first stage feed was about 65% catalytic cracked light gas oil with the remainder being atmospheric gas oil. The properties of the feed was as follows:

CARBON (WT%)	87.71
HYDROGEN (WT%)	12.21
SULPHUR (PPM)	29
NITROGEN (PPM)	14
DENSITY (15/4)	0.896

WT% AROMATIC CARBONS

BENZENES	12.9
NAPHTHALENES	2.9
PHENANTHRENES	1.0
TETRA	0.4
TOTAL	17.2

TBP-GC

WT% rec. (°C)

10	230
20	249
30	264
40	279
50	294
60	309
70	324
80	343
90	368
98	404

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5 The reactor was run for 22 days to obtain stability and the temperature of the reactor was recorded. As a reference catalyst was used a catalyst containing 3%wt. Ni and 9%wt W on a support made up of 80%wt zeolite USY and 20%wt alumina and made in the form of 0.32 cm cylinders. This catalyst is denoted Catalyst A in the table below. Other catalysts with differing sizes and differing amount of catalyst metals compared to the reference catalyst were tested and the activities in the form of reactor temperatures are indicated in the last two columns in the table below.

CATALYST	TYPE	EFFECTIVE DIAMETER		TOP BED SIMULATION*	FULL BED SIMULATION**
		CM	METALS		
A	cyl	0.37	reference	357 °C	345 °C
B	cyl	0.20	reference	350 °C	343 °C
C	cyl	0.20	2X Ni 1X W	344 °C	
D	cyl	0.20	2X Ni 2X W	346 °C	
E	cyl	0.20	1.5X Ni 1.5X W	347 °C	
F	trilobe	0.24	2X Ni 1X W	346 °C	
G	trilobe	0.16	2X Ni 1X W	342 °C	
H	trilobe	0.24	2.5X Ni 1.5X W	341 °C	

*LHSV of 6.0 hr⁻¹ and a conversion of 190 °C⁺ material of 12%
 **LHSV of 1.2 hr⁻¹ and a conversion of 190 °C⁺ material of 60%

10 As can be seen from the above data the reference catalyst A showed an activity loss in the top bed of 12 °C which would make it difficult to balance out the conversion across a five bed

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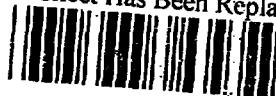


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second stage hydrocracker. Catalyst B, which has a smaller diameter, still has an activity problem. Simultaneously reducing the diameter and increasing the metals content provides a catalyst that solves the top bed problem.

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C L A I M S

1. Process for hydrocracking a hydrocarbonaceous feedstock having components boiling above 190 °C comprising reacting the feedstock in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions in a reactor which comprises at least two
5 separate beds of catalyst stacked on top of each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of
10 the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective particle diameter of the catalyst used in one or more of the top
15 beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.
2. Process according to claim 1, wherein the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds is 1.5 to 3 times the metals content of
20 the corresponding hydrogenation component of the catalyst used in the remaining beds.
3. Process according to claim 1 or 2, wherein the average effective particle diameter of the catalyst in the top bed is 0.25 to 0.75 times the average effective particle diameter of the
25 catalyst used in the remaining beds.
4. Process according to any one of claims 1-3, wherein the hydrogenation component comprises one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium.
- 30 5. Process according to claim 4, wherein the hydrogenation component of the catalyst in the remaining beds comprises between 1





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and 10% by weight of nickel and between 1 and 30% by weight of tungsten based on the total catalyst weight.

6. Process according to any one of claims 1-5, wherein the hydrogenation component(s) is (are) present in oxidic and/or sulphided form.
7. Process according to any one of claims 1-6, wherein the carrier is a molecular sieve having a pore diameter greater than 6 Å admixed with a binder comprising an inorganic oxide.
8. Process according to claim 7, wherein the molecular sieve is a zeolite Y and the binder comprises alumina, silica, silica-alumina or mixtures thereof.
9. Process according to claim 8, wherein the molecular sieve is an ultra-stable zeolite Y having a unit cell size of 24.20 to 24.60 Å.
10. Process according to any one of claims 1-9, wherein the catalyst in one or more of the top beds has the shape of a trilobe and the catalyst used in the remaining beds has the shape of a cylinder.
11. Process according to any one of claims 1-10, which is carried out at a temperature between 200 and 550 °C, a pressure between 35 and 350 bar and a liquid hourly space velocity of 0.1 to 10 volumes of liquid hydrocarbon per hour per volume of catalyst.

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HYDROCRACKING PROCESS

Process for hydrocracking a hydrocarbonaceous feedstock wherein use is made of a reactor comprising at least two separate beds of catalyst stacked on top of each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective particle diameter of the catalyst used in one or more of the top beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.

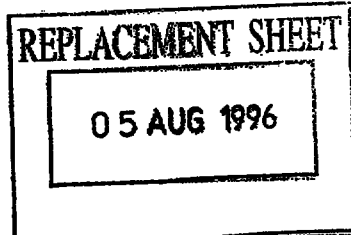
HYDROCRACKING PROCESS

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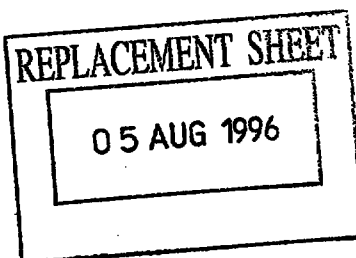


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sieves are generally suspended in a refractory inorganic oxide binder such as silica, alumina, or silica-alumina. The oxides such as silica, silica-alumina and alumina have also been used alone as the support for the hydrogenating metals for certain specific operations.

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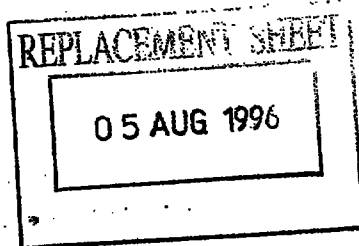
Hydrocracking is a general term which is applied to petroleum refining processes wherein hydrocarbonaceous feedstocks which have relatively high molecular weights are converted to lower molecular weight hydrocarbons at elevated temperature and pressure in the presence of a hydrocracking catalyst and a hydrogen-containing gas. Hydrogen is consumed in the cracking of the high molecular weight compounds to lower molecular weight compounds. Hydrogen will also be consumed in the conversion of any organic nitrogen and sulphur compound to ammonia and hydrogen sulphide as well as in the saturation of olefins and other unsaturated compounds. The hydrocracking reaction is exothermic and when substantially adiabatic reactors are used, as is usually the case, the temperature in the catalyst bed will rise progressively from the beginning to the end of the reactor. Excessive temperature in the reactor can present several problems. High temperatures can damage the catalyst, can result in the safe operating



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temperature of the reactor being exceeded or can cause the hydrocracking reaction to "run away", with disastrous results. This temperature rise problem can be solved by dividing the catalyst in the reactor into a series of beds with interstage cooling supplied between the beds by the injection of a cooled hydrogen-containing gas stream.

When a multiple bed configuration is used in a second stage hydrocracker, optimum use of the catalyst requires that each bed does a proportionate amount of the hydroconversion. For example in the commonly applied five bed second stage hydrocracker each bed should carry out about twenty percent of the hydroconversion, resulting in a temperature rise in each of the beds of about the same degree. It has now been found, however, that in many cases the catalyst in one or more of the first beds is somehow inhibited such that its activity is less than that of the catalyst in the remaining beds. As a result, the first bed carries out less than its proportionate share of hydroconversion, thus resulting in a smaller temperature rise in the first bed than occurs in the remaining beds. Raising the temperature of the feed to the first bed can increase conversion, but can also require excessive cooling between the first and second bed which will result in an inefficient utilization of hydrogen. Further, if the physical configuration of the reactor limits the amount of hydrogen that can be injected between the beds or limits the temperature to which the top bed can be heated, then the top bed can not be operated at its full hydroconversion potential. It has now been found that by modifying the catalyst in one or more of the first beds over that in the remaining beds by providing it with higher hydrogenation metals content and smaller particle size, the conversion in the first bed(s) can be raised to the level in the remaining beds, resulting in a more



efficient operation.

Accordingly, the present invention relates to a process for hydrocracking a hydrocarbonaceous feedstock having components boiling above 190 °C comprising reacting the feedstock in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions in a reactor which comprises at least two separate beds of catalyst stacked on top of each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective particle diameter of the catalyst used in one or more of the top beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.

The term "one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor" refers to the top bed and optionally the next bed or beds in series, without skipping, up to the point wherein the beds contain up to but not exceeding fifty percent by volume of the catalyst used in the reactor. For example, in a six bed reactor with catalyst equally disposed throughout the beds, "one or more of the top beds" will include (a) the top bed, (b) the top bed plus the second (from the top) bed and (c) the top bed plus the second bed plus the third (from the top) bed, but will not include the first bed and third bed (skipping the second bed). The top beds will thus be in contiguous series. The catalyst arranged in the

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aforementioned top beds will be referred hereinafter as the "top bed catalyst". The catalyst arranged in the remaining beds will be referred hereinafter as the "bottom bed catalyst". Suitably, the reactor has six or five beds. Preferably, the "one or more of the top beds" comprise the top bed and the bed next from the top bed. In another embodiment the "one or more of the top beds" include only the top bed.

The feedstock for the process comprises a heavy oil fraction having a major proportion, say, greater than fifty percent, of its components boiling above 190 °C, preferably above 220 °C or higher. Suitable feedstocks of this type include gas oils such as atmospheric and vacuum gas oils and coker gas oil, visbreaker oil, deasphalted oil, catalytic or thermal cracker cycle oils, synthetic gas oils, coker products and coal liquids. Normally the feedstock will have an extended boiling range, e.g., up to 590 °C or higher, but may be of more limited ranges with certain feedstocks. In general terms, the feedstocks will have a boiling range between about 150 °C and about 650 °C. Typically the feedstock has firstly been subjected to a hydroprocessing step prior to hydrocracking to remove nitrogen, sulphur and heavy metal impurities. This hydroprocessing step may also provide some degree of hydrocracking. The hydroprocessed feedstock may be passed directly to the hydrocracker, or it may be processed to remove ammonia, hydrogen sulphide and possibly lower boiling fractions prior to being passed to the hydrocracker.

Operating conditions to be used in the hydrocracking reaction zone include an average catalyst bed temperature within the range of 200 °C to 550 °C, preferably 260 °C to 480 °C, and most preferably 290 °C to 430 °C, a liquid hourly space velocity (LHSV) of 0.1 to 10 volumes of liquid hydrocarbon per hour per volume of catalyst,

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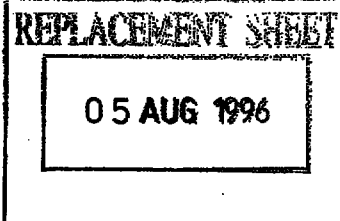
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preferably a LHSV of 0.5 to 5, and a total pressure within the range of 35 to 350 bar, a hydrogen partial pressure within the range of 35 and 310 bar, and a gas/feed ratio between 100 and 5000 Nl/kg feed.

The second stage hydrocracking reactor comprises a vertical reactor having from two to 6 beds of catalyst. Between the beds are placed means for injecting a hydrogen-containing stream into the reactor. This hydrogen-containing stream is cooler than the reactor, say, by 35 °C or more, and serves to cool the process stream as it passes from one bed to the one below. The hydrogen-containing stream may be pure hydrogen or may be admixed with other gases. Typically it is derived from hydrogen-rich processing streams such as those from hydrocarbon dehydrogenation reactors such as catalytic reformers or may be produced via steam-methane reforming. The hydrogen-containing stream is provided to each of the beds in amounts sufficient to maintain an excess of hydrogen throughout the reactor. The hydrocarbonaceous feedstock is heated to reactor temperature prior to being fed to the top bed. Typically, a hydrogen-containing stream is mixed with the feedstock and the mixture is heated to reaction temperature, although the hydrogen-containing stream may be fed separately to the top bed.

The catalysts used in the second stage hydrocracker may comprise metals, oxides and/or sulphides of Group VIB and/or Group VIII elements of the Periodic Table supported on a porous support having hydrocracking activity. The key aspect of the present invention is that the top bed catalyst will have a metals content higher and an effective diameter lower than that of the catalyst used in the remaining beds. The metals content of at least one of the hydrogenation components of the top bed catalyst will be 1.5, preferably 2 times the metals content of the corresponding hydrogenation components of



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the catalyst in the remaining beds when considered as the metal in terms of gram atoms per gram of total catalyst. Suitably the metals content of at least one of the hydrogenation components of the top bed catalyst will be 1.5 to 3, preferably from 1.5 to 2.5 times the metals content of the corresponding hydrogenation components of the catalyst in the remaining beds when considered as the metal in terms of gram atoms per gram of total catalyst. While reference is made herein to the "metals content" of the catalyst, it is understood that this is for measurement reference purposes and that the metal can be in other forms such as the oxide or sulphide. The gram atom per gram of total catalyst is determined by measuring the weight of metal in a gram of catalyst and dividing by the atomic weight of the metal. It is preferred that the catalysts in the beds other than the top bed, i.e., "the remaining beds", be substantially the same. However, it is contemplated that the remaining beds may individually contain catalysts that differ in metals content and average effective diameter, in which case reference to the metals content and average effective diameter of the catalyst in the remaining beds will refer to the maximum metals content and maximum average effective diameter of the catalysts used in the remaining beds.

In general when reference is made herein to the metals content of one or more hydrogenating components selected from Group VIB and Group VIII in the top bed(s) being greater than the content in the remaining bed(s), it is meant that the component in both the top and remaining or bottom beds will be the same component, that is, if the component is platinum in the bottom beds, then platinum will be in the top bed(s) in an increased amount. However, those with skill in the hydrocracking art will recognize that certain metals in Group VIB and

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Group VIII can be interchanged to provide comparable results. It is recognized in Group VIB that molybdenum and tungsten can be interchanged and in Group VIII that nickel and cobalt can be interchanged with each other and platinum and palladium can be interchanged with each other if their respective atomic weights are factored in. Thus, the instant specification and accompanying claims, as appropriate, recognize this equivalency and include the partial or complete substitution of molybdenum for tungsten (and vice versa), cobalt for nickel (and vice versa) and platinum for palladium (and vice versa) in the catalysts used in the top and bottom bed(s).

The average effective particle diameter of the top bed catalyst particles will be at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds. Suitably, the average effective particle diameter of the top bed catalyst particles will be 0.25 to 0.75 times the average effective particle diameter of the catalyst particles used in the remaining beds. Preferably, the particle shapes used in accordance with the present invention will be either cylinders or polylobes or both. The polylobed particles will have from two to five lobes. Trilobes are preferred for use in the top bed. The effective diameter of a particle is defined as the diameter of a sphere with the same surface to volume ratio (S/V) as the particle and can be calculated as 6 times V/S . Average effective particle diameters of catalyst used in the remaining beds will generally range from 0.13 to 0.51 cm. Cylinders are preferably used in the remaining beds.

The active metals component, "the hydrogenation component", of the hydrocracking catalyst is selected from a Group VIB and/or a Group VIII metal component. From Group VIB molybdenum, tungsten and mixtures thereof are preferred. From Group VIII there are two preferred

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classed: 1) cobalt, nickel and mixtures thereof and 2) platinum, palladium and mixtures thereof. Preferably both Group VIB and Group VIII metals are present. In a particularly preferred embodiment the hydrogenation component is nickel and/or cobalt combined with tungsten and/or molybdenum with nickel/tungsten being particularly preferred. The components are suitably present in the oxidic and/or sulphided form. In general the amounts of Group VIB and Group VIII metals present in the catalyst in the beds other than the top bed (the remaining beds) are set out below on an elemental basis and based on the total catalyst weight.

	<u>Suitably</u>	<u>Preferred</u>	<u>Most Preferred</u>
Group VIB	1-30	1-20	2-15
Group VIII	0.05-10	0.1-5	0.2-3.5
Nickel	1-10	1-5	1.5-3.5
Cobalt	1-6	1-5	1.5-4
Tungsten	1-30	2-20	4-15
Molybdenum	1-20	1-15	2-10
Platinum	0.05-5	0.1-2	0.2-1
Palladium	0.05-5	0.1-2	0.2-1

Suitably, the hydrogenation component of the catalyst in the remaining beds comprises between 1 and 10% by weight of nickel and between 1 and 30% by weight of tungsten based on the total catalyst weight. The Group VIB and Group VIII metals are supported on a carrier having hydrocracking activity. Two main classes of carriers known in the art typically include: (a) the porous inorganic oxide carriers selected from alumina, silica, alumina-silica and mixtures thereof and (b) the large pore molecular sieves. Mixtures of the inorganic oxide carriers and the molecular sieves can also be used. The term "silica-alumina" refers to non-

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zeolitic aluminosilicates.

Suitable supports are the large pore molecular sieves admixed with an inorganic oxide binder, preferably selected from the group consisting of alumina, silica, silica-alumina and mixtures thereof. The molecular sieves have pores greater than 6 Å, preferably between 6 to 12 Å. Suitable wide pore molecular sieves are described in the book Zeolite Molecular Sieves by Donald W. Breck, Robert E. Krieger Publishing Co., Malabar, Fla., 1984. Suitable wide pore molecular sieves comprise the crystalline aluminosilicates, the crystalline aluminophosphates, the crystalline silicoaluminophosphates and the crystalline borosilicates. Preferred are the crystalline aluminosilicates or zeolites. The zeolites are preferably selected from the group consisting of faujasite-type and mordenite-type zeolites. Suitable examples of the faujasite-type zeolites include zeolite Y and zeolite X. Other large pore zeolites such as zeolites L, beta and omega can also be used alone or in combination with the more preferred zeolites.

The most preferred support comprises a zeolite Y, preferably an ultrastable zeolite Y (zeolite USY). The ultrastable zeolites used herein are well known to those skilled in the art. They are for instance exemplified in U.S. Pat. Nos. 3,293,192 and 3,449,070. They are generally prepared from sodium zeolite Y by using one or more ammonium ion exchanges followed by steam calcination. They can further be subjected to a so-called dealumination technique to reduce the amount of alumina present in the system. Dealumination techniques are described extensively in the art and comprise inter alia the use of acid extraction, the use of silicon halides or other suitable chemical treating agents, chelates as well as the use of chlorine or chlorine-

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containing gases at high temperatures. They suitably have low sodium contents of less than 1 percent by weight and a unit cell size of 24.20 to 24.60 Å.

The zeolite is composited with an binder selected from alumina, silica, silica-alumina and mixtures thereof. Preferably the binder is an alumina binder, more preferably a gamma alumina binder or a precursor thereto, such as an alumina hydrogel, aluminum trihydroxide or aluminum oxyhydroxide.

Two classes of zeolite-containing supports are suitably used: (a) those containing a small amount of zeolite and a large amount of "binder", that is, alumina, silica, silica-alumina and mixtures thereof and (b) large amounts of zeolite and small amounts of binder.

The low zeolite-containing support will contain from 1 to 50, preferably from 1 to 25, and more preferably from 1 to 10 percent by weight of molecular sieve on a calcined (dehydrated) basis of molecular sieve plus binder with the balance being composed of binder.

The high zeolite-containing support suitably contains from 50 to 99, preferably from 60 to 95, and more preferably from 70 to 90 percent by weight of molecular sieve on a calcined (dehydrated) basis of molecular sieve plus binder with the balance being composed of binder.

The catalysts can be prepared by traditional methods. For example, the molecular sieve and binder in the form of a hydrogel or hydrosol may be mulled together with water and an optional peptizing agent, formed into extrudates and calcined. The calcined extrudates can be impregnated with one or more solutions containing solubilized salts of Group VIB and Group VIII elements. Alternatively, the hydrogenating components may be mulled into the zeolite/ alumina mixture prior to calcining. Impregnation and mulling may be combined as method for incorporating the hydrogenating components.

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The catalysts are normally presulphided prior to use. Typically, the catalysts are presulphided by heating in hydrogen sulphide/hydrogen atmosphere (e.g., 5%v H₂S/95%v H₂) at elevated temperatures, say 370 °C for several hours, e.g. 1-4 hours. Other methods are also suitable for presulphiding and generally comprise heating the catalysts to elevated temperatures (e.g., 204-398 °C) in the presence of hydrogen and sulphur or a sulphur-containing material.

The ranges and limitations provided in the present specification and claims are those which are believed to particularly point out and distinctly define the present invention. It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same way to obtain the same or substantially the same result are intended to be within the scope of the present invention as defined by the present specification and claims.

The present invention will now be described by the following examples.

EXAMPLES

In a commercial second stage hydrocracker having five beds of nickel-tungsten/zeolite USY-alumina catalyst in the shape of 0.32 cm cylinders it was found that the catalyst in the first or top bed was 8-10 °C less active than the catalyst in the lower beds. The reactor normally operates at a LHSV of 1.2 hour⁻¹ to provide a conversion of the feed boiling above 190 °C of 60%. The conversion is calculated from the formula:

$$\frac{[\%190\text{ }^{\circ}\text{C}^+(\text{feed}) - \%190\text{ }^{\circ}\text{C}^+(\text{product})] \times 100}{\%190\text{ }^{\circ}\text{C}^+(\text{feed})}$$

To model the second stage hydrocracker, a laboratory system was set up. This comprised a 1.9 cm I.D. reactor with a 0.64 cm thermowell running through the centre of the entire length of the 24.1 cm catalyst bed. To

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prepare the reactor, 20 cm³ of catalyst were diluted with 63 grams of 60x80 mesh silicon carbide and loaded into the reactor in four equally sized aliquots.

Catalyst was presulphided in the laboratory reactor by a programmed heating to 370 °C in 5%v/95%v H₂S/H₂ gas mixture flowing at 100 l/hr.

To model the full length hydrocracker (full bed), feed was provided to the reactor at a LHSV of 1.2 and the temperature was adjusted to provide a conversion of 60%. To model only the top bed of a five bed reactor, feed was provided to the reactor at a LHSV of 6 and the temperature was adjusted to give a conversion of 1/5 of the conversion in the full length reactor or 12%. The temperature of the reactor is a measure of the activity of the catalyst. The more active catalyst can be operated at a lower temperature than a less active catalyst while providing the same conversion.

The laboratory reactor conditions were:

Reactor inlet pressure	103.4 bar
LHSV	1.2* or 6.0** hr ⁻¹
hydrogen/oil ratio	1222 NL/kg
Conversion of 190 °C ⁺	60%* or 12%**

(*for full bed modeling; **for top bed modeling)

The feed used was a typical second stage hydrocracker feed fed to a commercial unit, containing recycle and was obtained while the hydrocracker was in the turbine fuel mode of operation. The corresponding first stage feed was about 65% catalytic cracked light gas oil with the remainder being atmospheric gas oil. The properties of the feed was as follows:

CARBON (WT%)	87.71
HYDROGEN (WT%)	12.21
SULPHUR (PPM)	29
NITROGEN (PPM)	14

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DENSITY (15/4) 0.896

WT% AROMATIC CARBONS

BENZENES	12.9
NAPHTHALENES	2.9
PHENANTHRENES	1.0
TETRA	0.4
TOTAL	17.2

TBP-GC

WT% rec. (°C)

10	230
20	249
30	264
40	279
50	294
60	309
70	324
80	343
90	368
98	404

The reactor was run for 22 days to obtain stability and the temperature of the reactor was recorded. As a reference catalyst was used a catalyst containing 3%wt. Ni and 9%wt W on a support made up of 80%wt zeolite USY and 20%wt alumina and made in the form of 0.32 cm cylinders. This catalyst is denoted Catalyst A in the table below. Other catalysts with differing sizes and differing amount of catalyst metals compared to the reference catalyst were tested and the activities in the form of reactor temperatures are indicated in the last two columns in the table below.

EFFECTIVE

DIAMETER

TOP BED

FULL BED

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<u>CATALYST</u>	<u>TYPE</u>	<u>CM</u>	<u>METALS</u>	<u>SIMULATION*</u>	<u>SIMULATION**</u>
A	cyl	0.37	reference	357 °C	345 °C
B	cyl	0.20	reference	350 °C	343 °C
C	cyl	0.20	2X Ni 1X W	344 °C	
D	cyl	0.20	2X Ni 2X W	346 °C	
E	cyl	0.20	1.5X Ni 1.5X W	347 °C	
F	trilobe	0.24	2X Ni 1X W	346 °C	
G	trilobe	0.16	2X Ni 1X W	342 °C	
H	trilobe	0.24	2.5X Ni 1.5X W	341 °C	

*LHSV of 6.0 hr^{-1} and a conversion of $190 \text{ }^{\circ}\text{C}^+$ material of 12%

**LHSV of 1.2 hr^{-1} and a conversion of $190 \text{ }^{\circ}\text{C}^+$ material of 60%

As can be seen from the above data the reference catalyst A showed an activity loss in the top bed of $12 \text{ }^{\circ}\text{C}$ which would make it difficult to balance out the conversion across a five bed second stage hydrocracker. Catalyst B, which has a smaller diameter, still has an activity problem. Simultaneously reducing the diameter and increasing the metals content provides a catalyst that solves the top bed problem.

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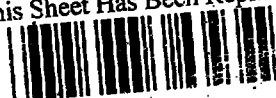


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T 2286 SINC L A I M S

1. Process for hydrocracking a hydrocarbonaceous feedstock having components boiling above 190 °C comprising reacting the feedstock in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions in a reactor which comprises at least two separate beds of catalyst stacked on top of each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective particle diameter of the catalyst used in one or more of the top beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.
2. Process according to claim 1, wherein the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds is 1.5 to 3 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds.
3. Process according to claim 1 or 2, wherein the average effective particle diameter of the catalyst in the top bed is 0.25 to 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.
4. Process according to any one of claims 1-3, wherein

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the hydrogenation component comprises one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium.

5. Process according to claim 4, wherein the hydrogenation component of the catalyst in the remaining beds comprises between 1 and 10% by weight of nickel and between 1 and 30% by weight of tungsten based on the total catalyst weight.

6. Process according to any one of claims 1-5, wherein the hydrogenation component(s) is (are) present in oxidic and/or sulphided form.

7. Process according to any one of claims 1-6, wherein the carrier is a molecular sieve having a pore diameter greater than 6 Å admixed with a binder comprising an inorganic oxide.

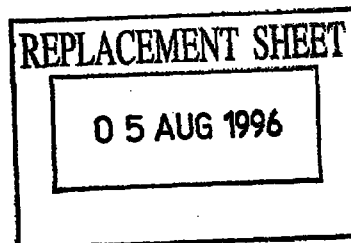
8. Process according to claim 7, wherein the molecular sieve is a zeolite Y and the binder comprises alumina, silica, silica-alumina or mixtures thereof.

9. Process according to claim 8, wherein the molecular sieve is an ultra-stable zeolite Y having a unit cell size of 24.20 to 24.60 Å.

10. Process according to any one of claims 1-9, wherein the catalyst in one or more of the top beds has the shape of a trilobe and the catalyst used in the remaining beds has the shape of a cylinder.

11. Process according to any one of claims 1-10, which is carried out at a temperature between 200 and 550 °C, a pressure between 35 and 350 bar and a liquid hourly space velocity of 0.1 to 10 volumes of liquid hydrocarbon per hour per volume of catalyst.

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T 2286 SINC L A I M S

1. Process for hydrocracking a hydrocarbonaceous feedstock having components boiling above 190 °C comprising reacting the feedstock in the presence of hydrogen with a hydrocracking catalyst under hydrocracking conditions in a reactor which comprises at least two separate beds of catalyst stacked on top of the feedstock being fed to the topmost bed, each other, which catalyst comprises one or more hydrogenation components of a Group VIB metal and/or Group VIII metal and a carrier having hydrocracking activity, whereby the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds comprising up to fifty percent by volume of the total catalyst used in the reactor is at least 1.5 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds and the average effective particle diameter of the catalyst used in one or more of the top beds is at most 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.
2. Process according to claim 1, wherein the metals content of at least one of the hydrogenation components of the catalyst used in one or more of the top beds is 1.5 to 3 times the metals content of the corresponding hydrogenation component of the catalyst used in the remaining beds.
3. Process according to claim 1 or 2, wherein the average effective particle diameter of the catalyst in the top bed is 0.25 to 0.75 times the average effective particle diameter of the catalyst used in the remaining beds.
4. Process according to any one of claims 1-3, wherein

