

## PROCESS FOR HYDROTREATING A HEAVY HYDROCARBON FRACTION WITH PERMUTABLE REACTORS AND REACTORS THAT CAN BE SHORT-CIRCUITED

The present invention relates to refining and converting heavy hydrocarbon fractions containing, inter alia, sulphur-containing and metallic impurities, such as atmospheric residues, vacuum residues, deasphalted oils, pitches, asphalts mixed with an aromatic distillate, coal hydrogenates, heavy oils of any origin and in particular those from bituminous schists or sands. In particular, it relates to treating liquid feeds. The scope of the invention also encompasses asphaltenes also being contained in the liquid feed.

Feeds which can be treated in accordance with the invention normally comprise at least 0.5 ppm by weight of metals (nickel and/or vanadium) and at least 0.5% by weight of sulphur.

The aim of catalytic hydrotreatment of such feeds is both to refine, i.e., to substantially reduce their metal, sulphur and other impurity contents while increasing the hydrogen-to-carbon ratio (H/C) while transforming them to a greater or lesser extent to lighter cuts, the different effluents obtained possibly serving as bases for the production of high quality fuel, gas oil and gasoline, or feeds for other units such as residue cracking or cracking vacuum distillates.

The problem with catalytic hydrotreatment of such feeds originates from the fact that such impurities gradually deposit themselves on the catalyst in the form of metals and coke, and tend to rapidly deactivate and clog the catalytic system, which necessitates a stoppage to replace it.

Processes for hydrotreating that type of feed must therefore be designed to allow as long as possible a cycle of operation without stopping the unit, the aim being to attain a minimum one year cycle of operation.

A variety of treatments for this type of feed exist. Such treatments have until now been carried out:

- either in processes using fixed catalyst beds (for example the HYVAHL-F process from the Institut Français du Pétrole);

- or in processes comprising at least one reactor enabling the catalyst to be replaced quasi-continuously (for example the HYVAHL-M moving bed process from the Institut Français du Pétrole).

The process of the present invention is an improvement over prior art processes, in particular  
5 fixed or ebullated bed processes. In such processes, the feed circulates through a plurality of reactors, preferably fixed or ebullated bed reactors, disposed in series, the first reactor or reactors being used to carry out hydrodemetallisation (HDM) of the feed in particular and part of the hydrodesulphurisation, the final reactor or reactors being used to carry out deep refining of the feed, and in particular hydrodesulphurisation (HDS step). The effluents are withdrawn from the last HDS  
10 reactor.

In such processes, specific catalysts adapted to each step are usually used, under average operating conditions of about 5 MPa to about 25 MPa, preferably about 10 MPa to about 20 MPa, and a temperature of about 370°C to 420°C.

For the HDM step, the ideal catalyst must be suitable for treating feeds which are rich in  
15 asphaltenes, while having a high demetallisation capacity associated with a high metal retention capacity and a high resistance to coking. The Applicant has developed such a catalyst on a particular macroporous support (the "sea urchin" structure) which endows it with precisely the desired qualities for this step (European patents EP-B-0 113 297 and EP-B-0 113 284):

- a degree of demetallisation of at least 10% to 90% in the HDM step;
- 20 • a metal retention capacity of more than 10% with respect to the weight of new catalyst, which results in longer cycles of operation;
- high resistance to coking even at temperatures of more than 390°C which contributes to extending the cycle period which is often limited by increasing the pressure drop and the activity

loss due to coke production, and which means that the majority of the thermal conversion can be carried out in this step.

For the HDS step, the ideal catalyst must have a high hydrogenating power so as to carry out deep refining of the products: desulphurisation, continuation of demetallisation, reducing the Conradson carbon and possibly the amount of asphaltenes. The Applicant has developed such a catalyst (EP-B-0 113 297 and EP-B-0 113 284) which is particularly suitable for treating that type of feed.

The disadvantage of that type of high hydrogenating capacity catalyst is that it rapidly deactivates in the presence of metals or coke. For this reason, combining a suitable HDM catalyst, which can function at a relatively high temperature to carry out most of the conversion and demetallisation, with a suitable HDS catalyst, which can be operated at a relatively low temperatures as it is protected from metals and other impurities by the HDM catalyst which encourages deep hydrogenation and limits coking, then in the end overall refining performances are obtained which are higher than those obtained with a single catalytic system or with those obtained with a similar HDM/HDS arrangement using an increasing temperature profile which leads to rapid coking of the HDS catalyst.

The importance of fixed bed processes is that high refining performances are obtained because of the high catalytic efficacy of fixed beds. In contrast, above a certain quantity of metals in the feed (for example 50 to 150 ppm), even though better catalytic systems are used, the performances and especially the operating period for such processes becomes insufficient: the reactors (in particular the first HDM reactor) rapidly become charged with metals and thus deactivate; to compensate for that deactivation, the temperatures are increased, which encourages coke formation and increases pressure drops; further, it is known that the first catalytic bed is susceptible to becoming clogged quite rapidly because of the asphaltenes and sediments contained in the feed or as a result of operating problems.

The result is that the unit has to be stopped a minimum of every 2 to 6 months to replace the first deactivated or clogged catalytic beds, that operation possibly lasting up to three weeks and further reducing the service factor of the unit.

The importance of ebullated bed processes is that the conversion performance is high due to the possibility of working at high temperatures. The Applicant has developed a process that is eminently suitable for treating conventional and heavy feeds (Canadian patent CA-2 171 894, French patent application FR-98/00530).

Although the best catalytic systems are used, the operation time can be reduced during problems in operations and/or during use not suited to the feed. The unit is thus stopped depending on how much coke is present in the reactor. We have attempted to solve these problems of operation and use of the catalyst.

We have also sought to overcome the disadvantages of fixed bed arrangements in different manners.

Thus, one or more moving bed reactors have been proposed, installed at the head of the HDM step (United States patents US-A-3 910 834 or British patent GB-B-2 124 252). Such moving beds can operate in co-current mode (the HYCON process from SHELL, for example) or in counter-current mode (the Applicant's HYVAHL-M process, for example). This protects the reactors, for example fixed bed reactors by carrying out part of the demetallisation and filtering the particles contained in the feed which could lead to clogging. Further, quasi-continuous replacement of the catalyst in that or those moving bed reactors avoids the need to stop the unit every 3 to 6 months.

The disadvantage of such moving bed techniques is that overall, their performances and efficiency are rather inferior to those for fixed beds of the same size, that they cause attrition of the circulating catalyst which can lead to obstruction of the fixed beds located downstream, and which above all, under the operating conditions used, the risks of coking and thus the formation of agglomerates of catalyst are far from negligible with such heavy feeds, in particular in the event of

problems. These agglomerates can prevent the catalyst from circulating either in the reactor or in the used catalyst withdrawal lines, and finally cause stoppage of the unit to clean the reactor and the withdrawal lines.

In order to retain excellent performance while maintaining an acceptable service factor, the addition of a guard reactor, preferably a fixed bed reactor (space velocity HSV = 2 to 4) in front of the HDM reactors has been considered (US-A-4 118 310 and US-A-3 968 026). Usually, this guard reactor can be short-circuited by using an isolation valve in particular. Thus the principal reactors are temporarily protected against clogging. When the guard reactor is clogged it is short-circuited, but then the following principal reactor can become clogged in its turn and lead to stoppage of the unit. Further, the small size of the guard reactor does not ensure a high degree of demetallisation of the feed and thus is a poor protector of the principal HDM reactors against the deposition of metals in the case of metal-rich feeds (more than 100 ppm, for example). Thus those reactors undergo accelerated deactivation leading to too frequent stoppages of the unit and thus to service factors which are still insufficient.

FR-B1-2 681 871 describes a system that combines good fixed bed performance with a high service factor for the treatment of feeds with a high metal content (1 to 1500 ppm but usually 100 to 1000 and preferably 150 to 350 ppm) which consists in a hydrotreatment process carried out in at least two steps to hydrotreat a heavy hydrocarbon fraction containing sulphur-containing impurities and metallic impurities in which in a first section, hydrodemetallisation, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions then in a subsequent second step, the effluent from the first section is passed over a hydrodesulphurisation catalyst under hydrodesulphurisation conditions. In this process, the hydrodemetallisation section comprises one or more hydrodemetallisation zones, preferably with fixed beds, preceded by at least two hydrodemetallisation guard zones, also preferably with fixed

beds, disposed in series for cyclic use consisting of successive repetition of steps b) and c) defined below:

- a) a step in which the guard zones are used together for a period at most equal to the deactivation time and/or clogging time for one thereof;
- 5 b) a step during which the deactivated and/or clogged guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh catalyst; and
- c) a step during which the guard zones are all used together, the guard zone where the catalyst has been regenerated during the preceding step being reconnected and said step being carried out for a period at most equal to the deactivation and/or clogging time for one of the guard zones.

10 This process produces a cycle period which is in general at least 11 months for the principal HDM and HDS reactors with high performances for refining and conversion while retaining the stability of the products. The overall desulphurisation is of the order of 90% and the overall demetallisation is of the order of 95%.

15 The disadvantage of this technology is the difficulty of obtaining overall desulphurisation performances of more than about 90% and/or overall demetallisation performances of more than about 95%, and the difficulty of obtaining cycle times of more than 11 months independent of performance levels. It has surprisingly been discovered that short-circuiting one or more reactors of the hydrodemetallisation and/or hydrodesulphurisation section can maintain the catalytic activity for each of the steps and/or improve the cycle time.

20 The present invention concerns the possibility of short-circuiting one or more reactors when the catalyst is deactivated and/or clogged by sediments or coke to be regenerated and/or replaced by fresh or regenerated catalyst. This invention concerns both reactors from the hydrodemetallisation section and reactors from the hydrodesulphurisation section.

It follows that the reactors from the hydrodemetallisation section and/or hydrodesulphurisation section are, for example, short-circuited every 6 months to replace the deactivated or clogged catalytic beds; this operation improves the service factor of the unit.

The invention consists in a process for hydrotreating a heavy hydrocarbon fraction in a first hydrodemetallisation section, then in a second hydrodesulphurisation section into which the effluent from the first section is passed. The hydrodemetallisation section is preceded by at least one guard zone. Said hydrotreatment process comprises the following steps:

- a) a step in which the guard zone is used;
- b) a step during which the guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced;
- c) a step during which the guard zone in which the catalyst has been regenerated and/or replaced is reconnected;
- d) a step in which at least one of the reactors from the hydrodemetallisation section and/or the hydrodesulphurisation section can be short-circuited and the catalyst it contains regenerated and/or replaced.

A route for improving fixed bed performance, summarised below, has also been described by the Applicant in FR-A-2 784 687. That concept can also be applied to the present invention.

However, there is some difficulty associated with the high viscosity of the feed and the total liquid effluent which causes high pressure drops in the reactor and difficulties in the operation of the recycling compressor, often resulting in a rather low hydrogen pressure which does not encourage either good hydrodemetallisation or good hydrodesulphurisation. Further, it has been shown that the gas oil fraction obtained normally cannot directly be used as its sulphur content is higher than current specifications allow.

It is desirable and possible to improve the performance of a process such as that described by the Applicant in French patents FR-B1-2 681 871 and FR-A-2 784 687. In particular, the process of

the present invention can very substantially reduce the viscosity of the liquid effluents, resulting in a substantial reduction in the pressure drops in the reactors, better operation of the recycling compressor and the production of a higher hydrogen pressure. This results in higher overall desulphurisation and a gas oil fraction with a much lower sulphur content, satisfying the current specifications and which can be directly used in the gas oil pool of the refinery. Further, in the process of the present invention, the preheat furnaces function better because of better heat transfer and thus the skin temperature of these furnaces is lower which helps to increase the service life of the furnaces and thus contributes to reducing the operating costs of the unit.

The process of the invention, which combines high performances of the reactors, preferably fixed bed reactors or ebullated bed reactors, with a high service factor for treating feeds with high metal contents (1 to 1500 ppm, but usually 100 to 1000 and preferably 150 to 350 ppm) can be defined in one of its variations as a process for hydrotreating, in at least two sections, a heavy hydrocarbon fraction containing sulphur-containing and metallic impurities in which, in a first, hydrodemetallisation, section, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions, then the effluent from the first section is passed over a hydrodesulphurisation catalyst in a subsequent second section under hydrodesulphurisation conditions, and in which the hydrodemetallisation section comprises one or more hydrodemetallisation zones, preferably fixed bed or ebullated bed zones, preceded by at least one or possibly two hydrodemetallisation guard zones, also preferably fixed bed or ebullated bed zones, disposed in series for use in a cycle consisting of successive repetitions of steps b) and c) defined below, the hydrodemetallisation and/or hydrodesulphurisation sections being composed of one or more reactors, preferably fixed bed or ebullated bed reactors, which can be short-circuited separately or otherwise following step d) defined below. When two guard zones are used, the process of the invention is a hydrotreatment process comprising:

- a) a step in which the guard zones are used all together for a period at most equal to the deactivation time and/or clogging time of one thereof;
- b) a step during which the deactivated and/or clogged guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh or regenerated catalyst;
- c) a step during which the guard zones are used all together, the guard zone in which the catalyst has been regenerated and/or replaced during the preceding step being reconnected and said step being carried out for a period at most equal to the deactivation and/or clogging time of one of the guard zones;
- d) a step in which at least one of the reactors from the hydrodemetallisation section and/or the hydrodesulphurisation section can be short-circuited during a cycle when the catalyst is deactivated and/or clogged for regeneration and/or replacement by fresh or regenerated catalyst.

A further variation of the process of the invention consists in a process for hydrotreating, in at least two sections, a heavy hydrocarbon fraction containing sulphur-containing and metallic impurities, in which in a first hydrodemetallisation, section, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions, then the effluent from the first step is passed over a hydrodesulphurisation catalyst in a subsequent second section under hydrodesulphurisation conditions, and in which the hydrodemetallisation section comprises one or more hydrodemetallisation zones preceded by at least one hydrodemetallisation guard zone, the hydrodemetallisation and/or hydrodesulphurisation sections being composed of one or more reactors which can be short-circuited separately or otherwise following step d) defined below, said hydrotreatment process comprising:

- a) a step in which the guard zone is used for a period at most equal to the deactivation time and/or clogging time of said zone;

- b) a step during which the deactivated and/or clogged guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh or regenerated catalyst;
- c) a step during which the guard zone in which the catalyst has been regenerated and/or replaced during the preceding step is reconnected, said step being carried out for a period at most equal to the deactivation and/or clogging time of one of the guard zones;
- d) a step in which at least one of the reactors from the hydrodemetallisation section and/or the hydrodesulphurisation section can be short-circuited during a cycle when the catalyst is deactivated and/or clogged for regeneration and/or replacement by fresh or regenerated catalyst.

In a variation of the process of the invention, the feed for said process is a heavy hydrocarbon fraction containing sulphur-containing and metallic impurities, in general at least 0.5 ppm by weight of metals, for example a fraction obtained by vacuum distillation, termed a vacuum distillate (VD).

Preferably, in the process of the invention, a quantity of middle distillate generally representing about 0.5% to about 80% by weight with respect to the weight of hydrocarbon feed is introduced into the first functioning guard zone.

More preferably, the quantity of middle distillate introduced represents about 1% to about 50%, by weight, highly preferably about 5% to about 25% by weight with respect to the weight of hydrocarbon feed.

In a particular implementation, the atmospheric distillate which is introduced with the hydrocarbon feed is a straight run gas oil.

In a further implementation, the product from the hydrodesulphurisation step is sent to an atmospheric distillation zone from which an atmospheric distillate is recovered at least a portion of

which is recycled to the inlet to the first functioning guard zone, and an atmospheric residue is recovered.

In a particular variation, at least a portion of a gas oil fraction from the atmospheric distillation is recycled. In this case, the gas oil cut which is recycled is usually a cut with an initial boiling point of about 140°C and with an end point of about 400°C. Usually this cut is a 150-370°C cut, or a 170-350°C cut.

In a further possible variation of the process of the invention, a gas oil from a unit functioning using the HYVAHL process can be recycled, or a light gas oil from a catalytic cracking unit, usually known as an LCO (light cycle oil) with an initial boiling point generally in the range about 140°C to about 220°C and an end point generally in the range about 340°C to about 400°C. It is also possible to recycle a fraction of heavy gas oil from catalytic cracking, usually termed an HCO (high cycle oil) with an initial boiling point in the range about 340°C to about 380°C and with a final boiling point generally in the range about 350°C to about 550°C.

The quantity of atmospheric distillate and/or gas oil which is recycled represents about 1% to 50%, preferably 5% to 25%, more preferably about 10% to 20% by weight, with respect to the feed.

In a further variation, at least a portion of the atmospheric residue from the atmospheric distillation zone is sent to a vacuum distillation zone from which a vacuum distillate is recovered at least a portion of which is recycled to the inlet to the first functioning guard zone, and a vacuum residue is also recovered which can be sent to the refinery fuel pool.

In a further variation, at least a portion of the atmospheric residue and/or vacuum distillate is sent to a catalytic cracking unit, preferably a fluidised bed catalytic cracking unit, for example a unit such as that using the R2R process developed by the Applicant. From this catalytic cracking unit, an LCO fraction and an HCO fraction in particular are recovered at least part of either one or the other, or a mixture of the two, can be added to the fresh feed which is sent to the hydrotreatment process of the present invention. Usually, a gas oil fraction, a gasoline fraction and a gaseous fraction are also

recovered. At least a portion of this gas oil fraction can optionally be recycled to the inlet to the first functioning guard zone.

The catalytic cracking step can be carried out in a conventional manner known to skilled persons under suitable residue cracking conditions to produce hydrocarbon-containing products with a lower molecular weight. Descriptions of the operation and catalysts which can be used in fluidised bed cracking can be found, for example, in US-A-4 695 370, EP-B-0 184 517, US-A-4 959 334, EP-B-0 323 297, US-A-4 965 232, US-A-5 120 691, US-A-5 344 544, US-A-5 449 496, EP-A-0 485 259, US-A-5 286 690, US-A-5 324 696 and EP-A-0 699 224 the descriptions of which are hereby incorporated into the present description by dint of their mention.

The fluidised bed catalytic cracking reactor can function in upflow or downflow mode. While this is not a preferred embodiment of the invention, it is also possible to carry out catalytic cracking in a moving bed reactor. Particularly preferred catalytic cracking catalysts are those which contain at least one zeolite usually mixed with an appropriate matrix such as alumina, silica or silica-alumina.

The process of the invention includes a particular variation in which during step c) the guard zones are used all together, the guard zone where the catalyst has been regenerated during step b) being reconnected such that its connection is identical to that which it had before it was short-circuited during step b).

The process of the invention comprises a further variation, which constitutes a preferred implementation of the present invention, comprising the following steps:

- a) a step in which the guard zones are all used together for a period at most equal to the deactivation and/or clogging time of the guard zone the most upstream with respect to the overall direction of circulation of the treated feed;
- b) a step during which the feed penetrates directly into the guard zone located immediately after that which was the most upstream during the preceding step and during which the guard zone

which was the most upstream during the preceding step is short-circuited and the catalyst which it contains is regenerated and/or replaced by fresh or regenerated catalyst; and

- c) a step during which the guard zones are used all together, the guard zone in which the catalyst has been regenerated and/or replaced during the preceding step being reconnected so as to be downstream of the set of guard zones and said step being continued for a period at most equal to the deactivation and/or clogging time of the guard zone which during this step is the most upstream with respect to the overall direction of circulation of the treated feed;
- d) a step in which at least one of the reactors from the hydrometallisation section and/or hydrodesulphurisation section can be short-circuited during the cycle when the catalyst is deactivated and/or clogged to be regenerated and/or replaced by fresh or regenerated catalyst.

In the preferred implementation of the process, the guard zone which is the most upstream in the overall direction of circulation of the feed gradually becomes charged with metals, coke, sediments and a variety of other impurities and is disconnected when desired but usually when the catalyst it contains is practically saturated with metals and various impurities.

In a preferred implementation, a particular conditioning section is used which permits permutation of these guard zones during operation, i.e., without stopping the unit's operation: firstly, a system which operates under moderate pressure (1 to 5 MPa but preferably 1.5 to 2.5 MPa) carries out the following operations on the disconnected guard reactor: washing, stripping, cooling, before discharging the used catalyst; then heating and sulphurisation after charging with fresh catalyst; then a further pressurisation/depressurisation and tap/valve system using appropriate technology effectively interchanges these guard zones without stopping the unit, i.e., without affecting the service factor, since all of the washing, stripping, discharging of used catalyst, recharging of fresh catalyst, heating and sulphurisation operations are carried out on the disconnected reactor or guard zone.

The reactors of the hydrotreatment unit usually function with the following hourly space velocities (HSV):

|                                            | HSV ( $\text{h}^{-1}$ ) | HSV ( $\text{h}^{-1}$ ) |
|--------------------------------------------|-------------------------|-------------------------|
|                                            | Broad range             | Preferred range         |
| Total HDM step: (including guard reactors) | 0.2 – 4.0               | 0.3 – 0.4               |
| Total HDS step:                            | 0.2 – 4.0               | 0.25 – 0.4              |
| Overall (HDM + HDS):                       | 0.10 – 2.0              | 0.12 – 0.30             |

The preferred mode consists of operating the guard reactors or zones in service at an overall HSV of about 0.1 to 4.0  $\text{h}^{-1}$ , usually about 0.2 to 1.0  $\text{h}^{-1}$ , which differs from other processes using smaller guard reactors, in particular as described in US-A-3 968 026 where smaller guard reactors are used. The value of the HSV of each functioning guard reactor is preferably about 0.5 to 8  $\text{h}^{-1}$  and usually about 1 to 2  $\text{h}^{-1}$ . The overall HSV of the guard reactors and that of each reactor is selected so as to carry out maximum hydrodemetallisation (HDM) while controlling the reaction temperature (limiting the exothermicity).

In an advantageous implementation, the unit comprises a conditioning section, not shown in the Figures, provided with circulation means, heating means, cooling means and suitable separation means functioning independently of the reaction section, whereby with the aid of lines and valves, the operations of preparing fresh or regenerated catalyst contained in the guard reactor and for the short-circuited reactor just before being connected, with the unit in operation, can be carried out, namely: pre-heating the guard reactor during permutation or short-circuiting, sulphurising the catalyst it contains, and bringing it to the required pressure and temperature conditions. When the permutation or short-circuiting operation of this guard reactor has been carried out using a set of suitable valves, this same section can also carry out the operations of conditioning the used catalyst contained in the guard reactor just after disconnection of the reaction section, namely: washing and stripping the used catalyst under the required conditions, then cooling before proceeding to the operations of discharging this used catalyst then replacing it with fresh or regenerated catalyst.

Preferably again, these catalysts are those described in the Applicant's patents EP-B-0 098 764 and the French patent filed with national registration number 97/07149. They contain a support and 0.1% to 30% by weight, expressed as the metal oxides, of at least one metal or compound of a metal of at least one of groups V, VI and VIII of the periodic table and in the form of a plurality of juxtaposed agglomerates each formed from a plurality of acicular platelets, the platelets of each agglomerate generally being radially orientated with respect to each other and with respect to the centre of the agglomerate.

More particularly, the present patent application concerns the treatment of heavy petroleum or petroleum fractions, with the aim of converting them into lighter fractions, that are easier to transport or treat using the usual refining processes. Oils from coal hydrogenation can also be treated. In this case, it is preferable to use ebullated bed reactors.

More particularly, the invention solves the problem of transforming a non transportable viscous heavy oil, which is rich in metals and sulphur, and contains more than 50% of constituents with a normal boiling point of more than 520°C to a stable hydrocarbon-containing product which can easily be transported, and having a reduced metals and asphaltenes content and a reduced content, for example less than 20% by weight, of constituents with a normal boiling point of more than 520°C.

In a particular implementation, before sending the feed to the guard reactors, it is first mixed with hydrogen and subjected to hydrovisbreaking conditions.

In a further implementation, the atmospheric residue or vacuum residue can undergo deasphalting using a solvent, for example a hydrocarbon-containing solvent or a solvent mixture. The most frequently used hydrocarbon-containing solvent is a paraffinic, olefinic or alicyclic hydrocarbon (or hydrocarbon mixture) containing 3 to 7 carbon atoms. This treatment is generally carried out under conditions that can produce a deasphalted product containing less than 0.05% by

weight of asphaltenes precipitated by heptane in accordance with the AFNOR NF T 60115 standard. This deasphalting can be carried out using the procedure described in the Applicant's patent US-A-4 715 946. The solvent/feed volume ratio will usually be about 3:1 to about 4:1 and the elementary physico-chemical operations which are comprised in the overall deasphalting operation (mixing-precipitation, decanting the asphaltene phase, washing-precipitation of the asphaltene phase) will usually be carried out separately. The deasphalted product is then normally at least partially recycled to the inlet to the first functioning guard zone.

Normally the solvent for washing the asphaltene phase is the same as that used for precipitation.

The mixture between the feed to be deasphalted and deasphalting solvent is usually carried out upstream of the exchanger which adjusts the temperature of the mixture to a value required to carry out proper precipitation and good decantation.

The feed-solvent mixture preferably passes into the tubes of the exchanger and not on the shell side.

The residence time of the feed-solvent mixture in the mixture precipitation zone is generally about 5 seconds (s) to about 5 minutes (min), preferably about 20 s to about 2 min.

The residence time for the mixture in the decanting zone is normally about 4 min to about 20 min.

The residence time for the mixture in the washing zone generally remains between about 4 min and about 20 min.

The rate of rise of the mixtures both in the decanting zone and in the washing zone are usually less than about 1 centimetre per second (cm/s), preferably less than about 0.5 cm/s.

The temperature applied in the washing zone is usually less than that applied in the decanting zone. The temperature difference between these two zones will normally be about 5°C to about 50°C.

The mixture from the washing zone will usually be recycled in the decanter and advantageously upstream of the exchanger located at the inlet to the decanting zone.

The solvent/asphaltene ratio recommended in the washing zone is about 0.5:1 to about 8:1 and preferably about 1:1 to about 5:1.

Deasphalting can comprise two stages, each stage including the three elementary phases of precipitation, decanting and washing. In this precise case, the temperature recommended in each phase of the first stage is preferably on average less than about 10°C to about 40°C at the temperature of each phase corresponding to the second stage.

The solvents which are used can also be C1 to C6 alcohols or phenols or glycol type solvents. However, paraffinic and/or olefinic solvents containing 3 to 6 carbon atoms are highly advantageously used.

In summary, in one variation, the process of the invention consists in a process for hydrotreating, in at least two sections, a heavy hydrocarbon fraction containing sulphur-containing and metallic impurities, in which in a first, hydrodemetallisation, section, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions, then the effluent from the first stage is passed over a hydrodesulphurisation catalyst in a subsequent second section under hydrodesulphurisation conditions, and in which the hydrodemetallisation section comprises one or more hydrodemetallisation zones preceded by at least two hydrodemetallisation guard zones disposed in series for use in a cycle consisting of successive repetitions of steps b) and c) defined below, the hydrodemetallisation and/or hydrodesulphurisation

sections being composed of one or more reactors which can be short-circuited separately or otherwise following step d) defined below, said hydrotreatment process comprising:

- a) a step in which the guard zones are used all together for a period at most equal to the deactivation time and/or clogging time of one thereof;
- b) a step during which the deactivated and/or clogged guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh or regenerated catalyst;
- c) a step during which the guard zones are used all together, the guard zone in which the catalyst has been regenerated and/or replaced during the preceding step being reconnected and said step being carried out for a period at most equal to the deactivation and/or clogging time of one of the guard zones;
- d) a step in which at least one of the reactors from the hydrodemetallisation section and/or the hydrodesulphurisation section can be short-circuited during a cycle when the catalyst is deactivated and/or clogged for regeneration and/or replacement by fresh or regenerated catalyst.

In a further variation, the process of the invention consists in a process for hydrotreating, in at least two sections, a heavy hydrocarbon fraction containing sulphur-containing and metallic impurities, in which in a first, hydrodemetallisation, section, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions, then the effluent from the first stage is passed over a hydrodesulphurisation catalyst in a subsequent second section under hydrodesulphurisation conditions, and in which the hydrodemetallisation section comprises one or more hydrodemetallisation zones preceded by at least one hydrodemetallisation guard zone, the hydrodemetallisation and/or hydrodesulphurisation sections being composed of one or more reactors which can be short-circuited separately or otherwise following step d) defined below, said hydrotreatment process comprising:

- a) a step in which the guard zone is used for a period at most equal to the deactivation time and/or clogging time of said zone;
- b) a step during which the deactivated and/or clogged guard zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh or regenerated catalyst;
- 5 c) a step during which the guard zone in which the catalyst has been regenerated and/or replaced during the preceding step is reconnected, said step being carried out for a period at most equal to the deactivation and/or clogging time of one of the guard zones;
- d) a step in which at least one of the reactors from the hydrodemetallisation section  
10 and/or the hydrodesulphurisation section can be short-circuited during a cycle when the catalyst is deactivated and/or clogged for regeneration and/or replacement by fresh or regenerated catalyst.

In a further variation, the process of the invention consists in a process for hydrotreating, in at least two sections, a heavy hydrocarbon fraction containing sulphur-containing and metallic  
15 impurities, in which in a first, hydrodemetallisation, section, the hydrocarbon feed and hydrogen are passed over a hydrodemetallisation catalyst under hydrodemetallisation conditions, then the effluent from the first section is passed over a hydrodesulphurisation catalyst in a subsequent second section under hydrodesulphurisation conditions, and in which the hydrodemetallisation section comprises one or more hydrodemetallisation zones preceded by at least two hydrodemetallisation guard zones  
20 comprising one or more reactors, preferably fixed bed or ebullated bed zones, disposed in series for use in a cycle consisting of successive repetitions of steps b) and c) defined below, the hydrodemetallisation and/or hydrodesulphurisation sections being composed of one or more reactors which can be short-circuited separately or otherwise following step d) defined below, said hydrotreatment process comprising:

- a) a step in which the guard zones are all used together for a period at most equal to the deactivation and/or clogging time of the guard zone the most upstream with respect to the overall direction of circulation of the treated feed;
- b) a step during which the feed penetrates directly into the guard zone located immediately after that which was the most upstream during the preceding step and during which the guard zone which was the most upstream during the preceding step is short-circuited and the catalyst which it contains is regenerated and/or replaced by fresh catalyst; and
- c) a step during which the guard zones are used all together, the guard zone in which the catalyst has been regenerated and/or replaced during step b) being reconnected so as to be downstream of the set of guard zones and said step being continued for a period at most equal to the deactivation and/or clogging time of the guard zone which during this step is the most upstream with respect to the overall direction of circulation of the treated feed;
- d) a step in which at least one of the reactors from the hydrodemetallisation section and/or hydrodesulphurisation section can be short-circuited during the cycle when the catalyst is deactivated and/or clogged to be regenerated and/or replaced by fresh or regenerated catalyst.

Preferably, in the process of the invention, a quantity of middle distillate generally representing 0.5% to 80% by weight with respect to the weight of hydrocarbon feed is introduced into the inlet to the first functioning guard zone. More preferably, the atmospheric distillate introduced with the hydrocarbon feed is a straight run gas oil.

In the process of the invention, the product from the hydrodesulphurisation step is preferably sent to an atmospheric distillation zone from which an atmospheric distillate is recovered at least a portion or which is preferably recycled to the inlet to the first functioning guard zone, and an atmospheric residue is also recovered. More preferably, at least a portion of a gas oil fraction from

the atmospheric distillation step following the hydrodesulphurisation step is recycled to the inlet to the first functioning guard zone.

In a preferred variation of the process of the invention, the recycled gas oil fraction is a cut with an initial boiling point of about 140°C and an end point of about 400°C.

5 In these preferred variations, the quantity of atmospheric distillate and/or gas oil introduced to the inlet to the first functioning guard zone at the same time as the feed preferably represents about 1% to 50% by weight with respect to the feed.

10 It is also possible to send at least a portion of the atmospheric residue from the atmospheric distillation zone to a vacuum distillation zone from which a vacuum distillate is recovered, at least a portion of which is recycled to the inlet to the first functioning guard zone, and a vacuum residue is also recovered. In this case, in a preferred variation, at least a portion of the atmospheric residue and/or vacuum distillate is sent to a catalytic cracking unit from which an LCO fraction and an HCO fraction are recovered, and at least a portion of one or the other or a mixture of the two fractions is sent to the inlet to the first functioning guard zone.

15 In a preferred mode of the process of the invention, during step c), the guard zones are used all together, the guard zone in which the catalyst has been regenerated during step b) being reconnected such that the connection is identical to that it had before it was short-circuited during step b).

20 In a further preferred mode of the process of the invention, a conditioning section is associated with the guard zone or zones, which section enables short-circuiting or permutation of said guard zone or zones during operation, without the unit ceasing operation, said section being regulated so as to condition the catalyst contained in the guard zone which is not functioning, at a pressure in the range 1 MPa to 5 MPa.

25 In a preferred mode of the process of the invention, in order to treat a feed constituted by a heavy oil or a heavy oil fraction containing asphaltenes, the feed is initially subjected to

hydrovisbreaking conditions, mixed with hydrogen, before sending the feed to the guard zone or zones.

In a preferred mode of the process of the invention, the atmospheric residue obtained from the optional atmospheric distillation step undergoes deasphalting using a solvent or a solvent mixture and at least a portion of the deasphalted product is recycled to the inlet to the first functioning guard zone.

In a preferred mode of the process of the invention, the vacuum residue obtained from the optional vacuum distillation step undergoes deasphalting using a solvent or solvent mixture and at least a portion of the deasphalted product is recycled to the inlet to the first functioning guard zone.

In a further preferred variation of the process of the invention, all of the reactors are fixed bed reactors. In a further preferred variation, at least one of the guard reactors and/or hydrodemetallisation sections and/or hydrodesulphurisation sections is an ebullated bed reactor. In a further preferred variation, the reactors for the guard zones are fixed bed reactors, and all of the reactors in the hydrodesulphurisation zone are ebullated bed reactors.

In a yet still further preferred variation, all of the reactors in the guard zone are fixed bed reactors, and all the reactors in the hydrodemetallisation zone are ebullated bed reactors, and optionally and highly preferably, all of the hydrodesulphurisation zone reactors are also ebullated bed reactors. It is also possible to operate the process of the invention with only ebullated bed reactors in the guard zones and in the hydrodemetallisation and hydrodesulphurisation sections.

Figure 1 briefly illustrates the invention.

The feed arrives in guard zones 1A and 1B via line 1 and leaves these zones via line 13, line 23 and/or line 24. The feed leaving the guard zone or zones arrives via line 13 in the HDM section which is shown here by a reaction section 2 constituted by one or more reactor(s), each reactor being provided with its own short-circuit. The effluent from section 2 is withdrawn via line 14 then sent to a hydrodesulphurisation section 3 which can comprise one or more reactors that may be in series,

and my optionally be provided with their own short-circuit. The effluent from section 3 is withdrawn via line 15.

In the illustration of Figure 1, a middle distillate is introduced via line 55 and is mixed with the hydrocarbon feed in line 1.

5 In the case shown in Figure 1, the guard zone comprises 2 reactors; in its preferred implementation, the process will comprise a series of cycles each comprising four successive periods:

- 10 • a first period during which the feed successively traverses zone 1A then zone 1B and in which the gas oil fraction from atmospheric distillation which is recycled is introduced with the feed into zone 1A; during the first period [step a) of the process], the feed is introduced via line 1 and line 21 comprising a valve 31 open towards the guard reactor 1A. During this period, valves 32, 33 and 35 are closed. The effluent from zone 1A is sent via a line 23, line 26, comprising an open valve 34 and line 22 to guard reactor 1B. The effluent from zone 1B is sent via line 24, comprising an open valve 36, and line 13, which comprises an open valve 37, to HDM section 2.
- 15 • a second period during which the feed traverses only zone 1B and in which the gas oil fraction from atmospheric distillation which is recycled is introduced with the feed into zone 1B. During the second period [step b) of the process], valves 31, 33, 34 and 35 are closed and the feed is introduced via line 1 and line 22, comprising an open valve 32, into zone 1B. During this period the effluent from zone 1B is sent via line 24 comprising an open valve 36 and line 13, which  
20 comprises an open valve 37 to HDM section 2;
- a third period during which the feed successively traverses zone 1B then zone 1A and in which the gas oil fraction from atmospheric distillation which is recycled is introduced into zone 1B with the feed. During the third period [step c) of the process], valves 31, 34 and 36 are closed and valves 32, 33 and 35 are open. The feed is introduced via line 1 and line 22 into zone 1B.

The effluent from zone 1B is sent via line 24, line 27 and line 21 to guard reactor 1A. The effluent from zone 1A is sent via line 23 and line 13, which comprises an open valve 37, to HDM section 2;

- a fourth period during which the feed only traverses guard zone 1A and in which the gas oil fraction from atmospheric distillation which is recycled is introduced into zone 1A with the feed.

The number of cycles carried out for the guard reactors is a function of the duration of the operating cycle of the whole unit and the average frequency of permutation of zones 1A and 1B. During the fourth period, valves 32, 33, 34 and 36 are closed and valves 31 and 35 are open. The feed is introduced into zone 1A via line 1 and line 21. During this period, the effluent from zone 1A is sent to HDM section 2 via line 23 and line 13 which comprises an open valve 37.

In the case shown in Figure 1, hydrodemetallisation (HDM) section 2 can comprise one or more reactors. Each or a plurality of these reactors can be temporarily isolated for periodic renewal of the catalyst(s) [step d) of the process]. In its preferred implementation, the process comprises a series of cycles each comprising three successive periods:

- a first period during which the feed successively traverses guard zones 1A, 1B and HDM section 2, then finally HDS section 3. During this period, the gas oil fraction from atmospheric distillation which is recycled is introduced into guard zone 1A with the feed. During this period, valves 32, 33, 35, 38 and 41 are closed. The feed is introduced into zone 1A via line 1 and line 21. The effluent from zone 1A is sent to guard zone 1B via a line 23, line 26, comprising an open valve 34 and line 22. The effluent from zone 1B is sent to HDM section 2 via line 24, comprising an open valve 36, and line 13, which comprises an open valve 37. The effluent from section 2 is sent to HDS section 3 via line 14 which comprises two open valves 42 and 39. The effluent from section 3 is then sent to a fractionation unit (not shown) via line 15 which comprises an open valve 40.

- a second period during which the feed successively traverses guard zones 1A and 1B, then HDS section 3. During this period, the gas oil fraction from atmospheric distillation which is recycled is introduced into zone 1B with the feed. During this operation, valves 32, 33, 35, 37, 41 and 42 are closed. The feed is introduced into zone 1A via line 1 and line 21. The effluent from zone 1A is sent to guard zone 1B via line 23, line 26 which comprises an open valve 34, and line 22. The effluent from zone 1B is sent to HDS section 3 via line 24, which comprises an open valve 36, and line 25 which comprises two open valves 38 and 39. The effluent from section 3 is then sent to fractionation unit (not shown), via line 15, which comprises an open valve 40. During this period, the HDM catalyst is renewed, then said catalyst is conditioned using the method described in this invention. This conditioning is particularly necessary if the catalyst is in the oxide form;
- a third period during which the feed successively traverses guard zones 1A and 1B, and HDM section 2, then HDS section 3. During this period, the gas oil fraction from the atmospheric distillation step which is recycled is introduced with the feed into guard zone 1B. This situation is identical to the first period and allows the reactor containing the fresh catalyst to be replaced in an identical position, in the fluid circuit, compared with that described in the first period.

In the case represented in Figure 1, hydrodesulphurisation section 3 can comprise one or more reactors; each or a plurality of these reactors can be temporarily isolated to renew the catalyst periodically [step d) of the process]. In its preferred implementation, the process comprises a series of cycles each comprising three successive periods:

- a first period during which the feed successively traverses guard zones 1A, 1B and HDM section 2, then HDS section 3. During this period, the gas oil fraction from atmospheric distillation which is recycled is introduced with the feed into guard zone 1A. During this period, valves 32, 33, 35, 38 and 41 are closed. The feed is introduced into guard zone 1A via line 1 and line 21.

The effluent from guard zone 1A is sent to guard zone 1B via line 23, line 26, comprising an open valve 34 and line 22. The effluent from guard zone 1B is sent to HDM section 2 via line 24, comprising an open valve 36, and line 13, which comprises an open valve 37. The effluent from section 2 is sent to section 3 via line 14 which comprises two open valves 42 and 39. The effluent from section 3 is then sent to a fractionation unit (not shown) via line 15 which comprises an open valve 40.

- a second period during which the feed successively traverses guard zones 1A and 1B, then HDM section 2. During this period, the gas oil fraction from atmospheric distillation which is recycled is introduced with the feed into zone 1B. During this operation, valves 32, 33, 35, 38, 39 and 40 are closed. The feed is introduced into zone 1A via line 1 and line 21. The effluent from zone 1A is sent to zone 1B via line 23, line 26 which comprises an open valve 34, and line 22. The effluent from zone 1B is sent to HDM section 2 via line 24, which comprises an open valve 36, and line 13 which comprises an open valve 37. The effluent from section 2 is then sent to fractionation unit (not shown), via line 14, which comprises an open valve 42, and line 16, which comprises an open valve 41. During this period, the catalyst or catalysts from section 3 are renewed, then said catalyst or catalysts are conditioned using the method described in this invention. This conditioning is particularly necessary when the catalyst is in the oxide form;
- a third period during which the feed successively traverses guard zones 1A and 1B, and HDM section 2, then HDS section 3. During this period, the gas oil fraction from the atmospheric distillation step which is recycled is introduced into zone 1B with the feed. This situation is identical to that described in period 1 and allows the reactor containing the fresh catalyst(s) to be replaced in the same position, in the fluid circuit, as that described in the first period.

## Claims

1. Process for hydrotreatment, in at least two sections, of a heavy hydrocarbon fraction containing sulphur-containing impurities and metallic impurities, in which in a first section called a hydrodemetallization section the charge of hydrocarbons and hydrogen is passed, under hydrodemetallization conditions, over a hydrodemetallization catalyst, and then in a subsequent second section, the effluent from the first step is passed under hydrodesulphurization conditions over a hydrodesulphurization catalyst, and in which the hydrodemetallization section comprises one or more hydrodemetallization zones preceded by at least one guard zone, the hydrodesulphurization section being composed of a plurality of reactors which can be short-circuited separately or otherwise in accordance with step d) defined hereinafter, the said hydrotreatment process comprising:

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- a) a step, in which the guard zone or zones are used for a period at most equal to the deactivation and/or clogging time of the said zone,
- b) a step, during which a deactivated and/or clogged guard zone is short-circuited and the catalyst which it contains is regenerated and/or replaced by fresh or regenerated catalyst,
- c) a step, during which the guard zone, the catalyst of which was regenerated and/or replaced during the preceding step, is reconnected, the said step being continued for a period at most equal to the deactivation and/or clogging time of a guard zone,
- d) a step in which at least one of the reactors of the hydrodesulphurization section can be short-circuited during the cycle when the catalyst is

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deactivated and/or clogged to be regenerated and/or replaced by fresh or regenerated catalyst.

2. Process for hydrotreatment as described in claim 1,  
5 in which the said hydrodemetallization zone or zones are preceded by at least two hydrodemetallization guard zones arranged in series to be used in cyclic manner consisting of the successive repetition of steps b) and c), and in which the guard zones are all used together during the  
10 said steps a) and c) for a period at most equal to the deactivation and/or clogging time of one of them.

3. Process for hydrotreatment as described in claim 2,  
in which the said hydrodemetallization guard zones  
15 comprise one or more fixed bed or bubbling bed reactors and in which, during step c), the guard zones are all used together, the guard zone the catalyst of which was regenerated and/or replaced during the preceding step b) being so reconnected as to be downstream of all the guard  
20 zones, the said step being continued for a period at most equal to the deactivation and/or clogging time of the guard zone which is, during this step, the most upstream relative to the general direction of circulation of the treated charge.

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4. Process as described in one of claims 1 to 3, in which, at the same time as the charge, at the intake of the first functioning guard zone, a quantity of medium distillate is introduced representing 0.5% to 80% by  
30 weight relative to the weight of the hydrocarbon charge.

5. Process as described in claim 4 in which the atmospheric distillate introduced with the hydrocarbon charge is a straight run gas-oil.

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6. Process as described in one of claims 1 to 5, in which the product from the hydrodesulphurization step is sent into an atmospheric distillation zone from which is recovered an atmospheric distillate, at least a part of which is recycled to the intake of the first functioning guard zone, and an atmospheric residue.

7. Process as described in claim 6, in which at least a part of a gas-oil fraction from the atmospheric distillation which follows the hydrodesulphurization step is recycled to the intake of the first functioning guard zone.

8. Process as described in claim 5 or 7, in which the gas-oil fraction is a cut with an initial boiling point of approximately 140°C and end point of approximately 400°C.

9. Process as described in one of claims 4 to 8, in which the quantity of atmospheric distillate and/or gas-oil introduced at the intake of the first functioning guard zone at the same time as the charge represents approximately 1 to 50% by weight relative to the charge.

10. Process as described in one of claims 6 or 7, in which at least a part of the atmospheric residue from the atmospheric distillation zone is sent into a vacuum distillation zone from which is recovered a vacuum distillate, at least a part of which is recycled to the intake of the first functioning guard zone, and a vacuum residue.

11. Process as described in claim 10, in which at least a part of the atmospheric residue and/or of the vacuum distillate is sent into a catalytic cracking unit from which is recovered an LCO fraction and an HCO fraction

15 AUG 2003

which are sent, at least partially, either the one or the other or a mixture of the two, to the intake of the first functioning guard zone.

5 12. Process as described in one of claims 1 and 3, in which during step c) the guard zones are all used together, the guard zone the catalyst of which was regenerated during step b) being so reconnected that its connection is identical to that which it had before it  
10 was short-circuited during step b).

13. Process as described in one of claims 1 to 12 in which with the guard zone or zones is associated a conditioning section which allows running short-  
15 circuiting or permutation of the said guard zone or zones, without stopping the operation of the unit, the said section being so controlled as to condition the catalyst contained in the guard zone which is not functioning, at a pressure of between 1 MPa and 5MPa.

20 14. Process as described in one of claims 1 to 13, in which, in order to treat a charge formed of a heavy oil or of a heavy oil fraction containing asphaltenes, the charge is firstly subjected to hydrovisbreaking  
25 conditions, mixed with hydrogen, before the charge is sent into the guard zone or zones.

15. Process as described in one of claims 7, 10, or 11, in which the atmospheric residue is subjected to  
30 deasphalting with a solvent or a solvent mixture and the deasphalted product is at least partially recycled to the intake of the first functioning guard zone.

16. Process as described in one of claims 10 or 11, in  
35 which the vacuum residue is subjected to deasphalting with a solvent or a solvent mixture and the deasphalted

15 AUG 2003

product is at least partially recycled to the intake of the first functioning guard zone.

17. Process as described in one of claims 1 to 16 in which all the reactors are fixed bed.

18. Process as described in one of claims 1 to 17, in which at least one reactors of the guard zones and/or of the hydrodemetallization and/or hydrodesulphurization sections is a bubbling bed reactor.

19. Process as described in claim 18, in which all the reactors of the guard zones are fixed bed and all the reactors of the hydrodesulphurization zone are bubbling bed.

20. Process as described in claim 18 or 19, in which all the reactors of the guard zones are fixed bed and all the reactors of the hydrodemetallization zone are bubbling bed.

15 AUG 2003

Translator's note

Claim 18: "at least one reactors", sic.