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HYDROCONVERSION OF HEAVY OILS  
THROUGH EBULLATED-BED SYSTEMS**(30) **Foreign Application Priority Data**

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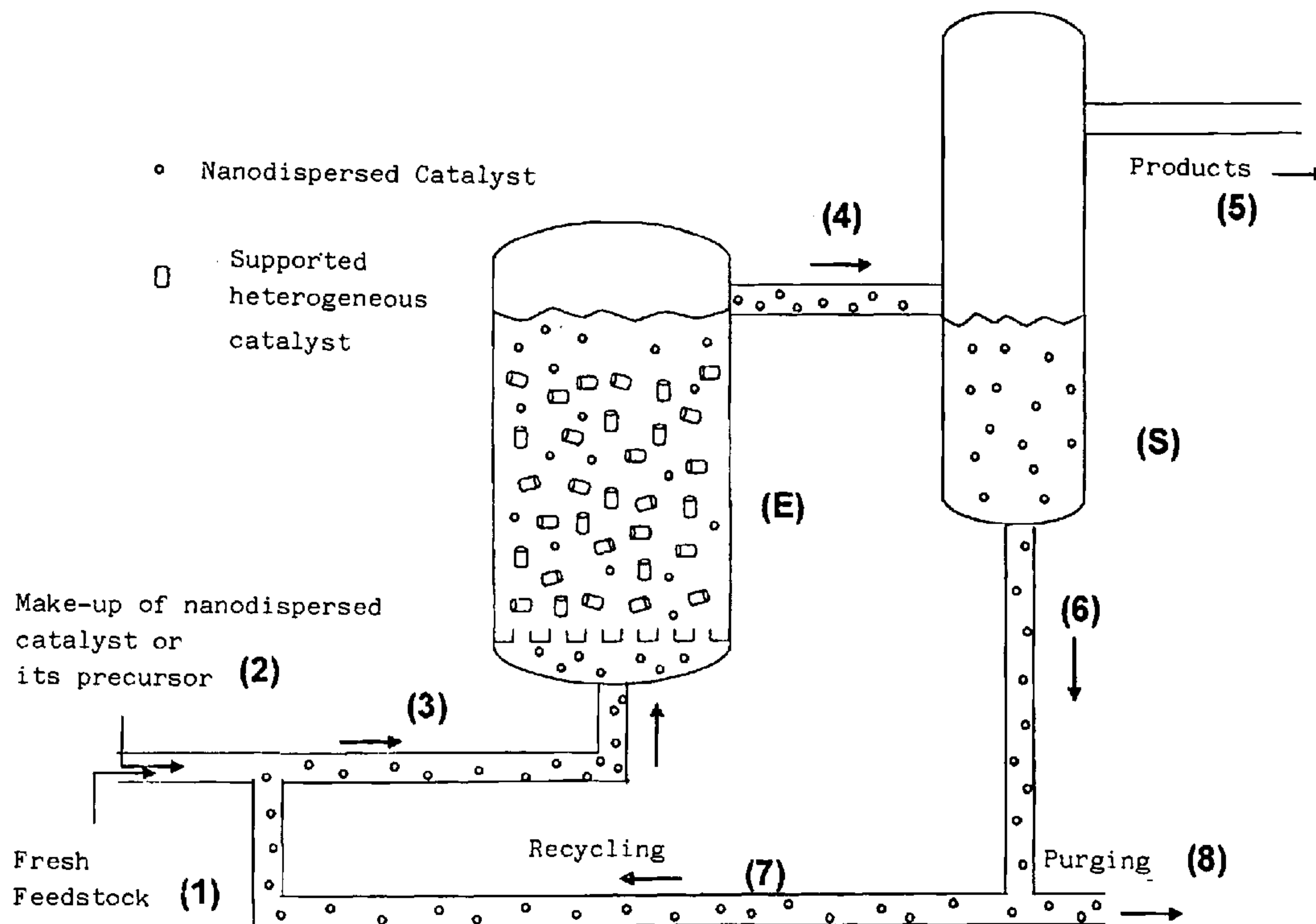
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**ALEXANDRIA, VA 22314 (US)**(73) Assignee: **ENI S.P.A.**, Rome (IT)(21) Appl. No.: **12/664,474**(22) PCT Filed: **Jun. 9, 2008**(86) PCT No.: **PCT/EP2008/004680**

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(2), (4) Date: **Apr. 16, 2010**(57) **ABSTRACT**

Process for the hydroconversion of heavy oils, selected from crude oils, heavy crude oils, bitumens from tar sands, distillation residues, distillation heavy cuts, distillation deasphalted residues, vegetable oils, oils from coal and oil shale, oils from the thermodecomposition of waste material, polymers, biomasses, comprising sending the heavy oil to a hydroconversion area, effected in one or more ebullated bed reactors, wherein hydrogen is introduced, in the presence of a suitable heterogeneous, supported, hydroconversion catalyst, in addition to a suitable hydrogenation catalyst, nano-dispersed in said heavy oil, and sending the stream coming from the hydroconversion area to a separation area, in which the separated liquid fraction, containing the nano-dispersed catalyst, is recycled to the ebullated bed reactor(s).



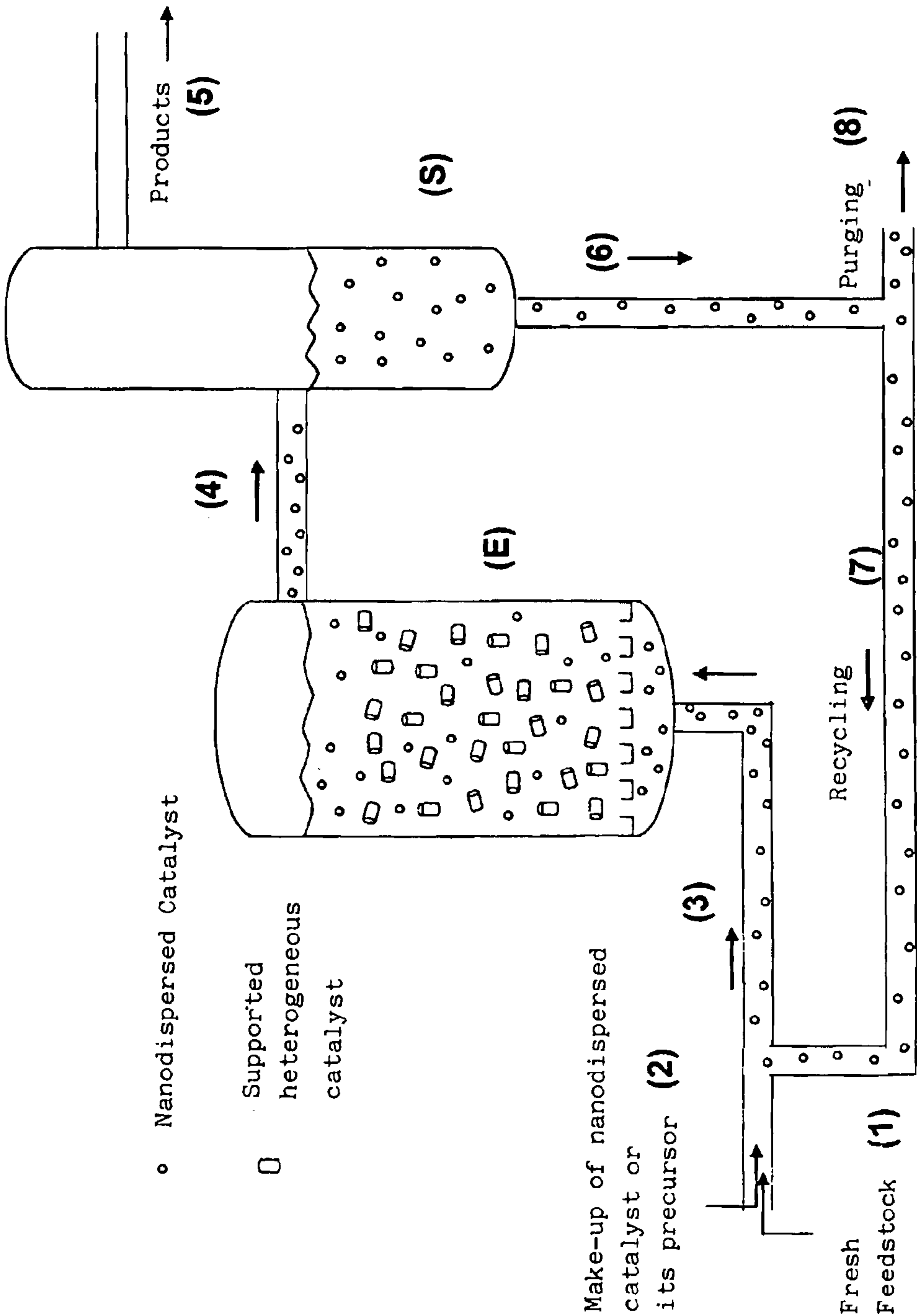


Fig. 1



# **ENHANCED PROCESS FOR THE HYDROCONVERSION OF HEAVY OILS THROUGH EBULLATED-BED SYSTEMS**

**[0001]** The present invention describes an enhanced process for the hydroconversion of heavy oils through ebullated-bed systems.

**[0002]** In processes used for the hydroconversion of heavy hydrocarbon residues, the feedstock to be treated is put in contact with hydrogen in the presence of a hydrogenation catalyst under suitable temperature and pressure conditions. The conversion degree for each single passage is never total. On the contrary, it is far from being so, to the extent that, in industrial practice, it is necessary for at least two reactors to be put in series in order to obtain a conversion degree of 70%. The non-converted fraction of the feedstock is inevitably destined for fuel oils or other equivalent uses of little economical interest and at times creating environmental problems.

**[0003]** In this area, the upgrading ebullated-bed technologies of heavy residues have improved the pre-existing fixed-bed technologies due to a higher efficiency of the catalyst, a better thermal and material exchange. The supported heterogeneous catalyst, in pellets having a suitable form and with millimetric dimensions, is suspended in the hydrocracking reactor, mainly regulating the liquid flow by means of the feeding flow-rate of the feedstock and through a recycling pump of the liquid, inside or outside the reactor. The flow-rates are regulated so that the catalyst is positioned in a central area of the reactor, delimited by a liquid seal at the inlet and outlet of the reactor. The reaction is of the once-through type, with no recycling and the reaction products are gas, naphtha, gas oil, vacuum gas oil (VGO) and fuel oil. The typical reaction conditions of a hydrocracking process with an ebullated-bed reactor, (see, for example, "Oil & Gas Science and Technology, Rev. IFP, Vol. 55, 2000, Nr. 4, p. 397") are indicated in the following table:

Reaction conditions	standard	preferred
Residue content 975° F. <sup>+</sup> in the feedstock (w %)	50-100	80-100
LHSV (liquid hourly space velocity) hr <sup>-1</sup>	0.1-1.0	0.2-0.5
Reactor temperature ° F.	700-850	770-820
Partial pressure, psig	500-3,500	2,500-3,000
H <sub>2</sub> partial pressure at the reactor outlet, psi	1,500-2,500	1,800-2,100
Catalyst make-up rate lb/bbl	0.03-1.0	0.05-0.60

**[0004]** Even if the ebullated-bed technology has improved fixed-bed technologies, it still has various restrictions, as it produces fuel oil.

**[0005]** The catalyst used in ebullated-bed technologies normally consists of alumina as binder and two active phases, one responsible for the cracking activity and which can be introduced by acting on the composition of the binder (for example, SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> or blends thereof) or by adding a second material having acidic sites (clay or zeolites, for example) and one responsible for the hydrogen transfer activity, obtained by functionalization of the carrier with a suitable mixture of Mo(W)/Co(Ni)sulphides. This catalyst has a good hydrocracking capacity and a sufficient capacity for activating

the molecular hydrogen and blocking the free radicals and formation of pitchy products which can cause a rapid deterioration of the catalyst or the obstruction of some of the plant sections. The limited hydrogen activation capacity, however, does not allow the heaviest reaction products to be recycled, thus limiting the conversion and causing the undesired production of fuel oil. Furthermore, for the same reasons, the concentrations of solid products (above all coke and its precursors) in the reaction means, must be maintained at low levels. In ebullated-bed processes, the solid hold-up (evaluate by means of the HFT Hot Filtration Test technique) is lower than about 0.2% and frequent maintenance interventions are necessary for removing the pitchy deposits formed in various areas of the plant.

**[0006]** As an alternative to hydroconversion processes based on the use of catalysts supported on fixed or ebullated beds, processes have also been proposed using homogeneously dispersed catalysts in the reaction means (slurry). These "slurry" processes are characterized by the presence of catalyst particles having very small average dimensions, micronic and/or sub-micronic and uniformly dispersed in the hydrocarbon phase.

**[0007]** The catalyst normally used in slurry processes consists of a nano-dispersion of laminar crystallites of molybdenite (MoS<sub>2</sub>), produced in-situ in the reaction means, starting from an oil-soluble compound fed together with the feedstock (see, for example, IT-M12003A000692 and IT-MI2003A000693) or ex-situ, by the interaction of a suitable molybdenum compound with H<sub>2</sub>S or an organic sulphide. This material is highly efficient in the activation of hydrogen and has optimum properties as a scavenger of radicals (Applied Catalysis A: General, 204, 2000, p. 203). The main function of this material, in fact, is to limit the formation of resins or pitches from organic compounds having a low H/C ratio, by blocking and limiting the diffusion of free radicals in the reaction means, thus preventing the formation of coke. Molybdenite, however, has a low cracking capacity and consequently in slurry processes the cracking is mainly of a thermal nature (Applied Catalyst A: General, 204, 2000, page 215).

**[0008]** Furthermore, the catalyst activity is hardly influenced by the presence of carbonaceous residues coming from the degradation of asphaltenes.

**[0009]** The possibility of enhancing ebullated-bed technologies by adding a nano-dispersed catalyst based on MoS<sub>2</sub> to the reaction system, so that the concentration of the latter ranges from 10 to 500 ppm with respect to the feed-stock, has also been proposed in literature (EP-546686 of Texaco Dev. Corp., US 2005/0241991 of Headwaters Heavy Oil LLC). The other process conditions are similar to those of ebullated-bed processes: there is no recycling of the heavy fraction and therefore fuel oil is still present in the reaction products, even if the quality of bottom hydrocracking has improved in terms of density with respect to the starting case. In once-through configurations, the concentration of molybdenite in the reaction means must be kept low as, in the absence of recycling, the catalyst is used up.

**[0010]** In conclusion, even if improvements have been observed with respect to a typical ebullated-bed configuration, the main problems of this technology have not been completely solved.

**[0011]** A process has now been surprisingly found, which can be applied to heavy oils, selected from crude oils, heavy crude oils, bitumen from tar sands, distillation residues, dis-



tillation heavy cuts, deasphalted distillation residues, vegetable oils, oils from coal and oil shale, oils from the thermal decomposition of waste material, polymers, biomasses, which is such as to substantially overcome the problems so far found in ebullated-bed hydrocracking processes for the conversion of heavy residues to distillates, by modifying the typical scheme of an ebullated-bed process by adding a recycling section to the reactor of the non-converted heavy portion obtained from the bottom of a distillation column or other liquid/vapour separation unit.

**[0012]** The process, object of the present invention, for the hydroconversion of heavy oils, includes sending the heavy oil to a hydroconversion area effected in one or more ebullated-bed reactors into which hydrogen is introduced, in the presence of a suitable heterogeneous, supported, hydroconversion catalyst and a suitable hydrogenation catalyst, nano-dispersed in said heavy oil, and sending the effluent stream from the hydroconversion area to a separation area in which the liquid fraction separated, containing the nano-dispersed catalyst, is recycled to the reactor(s).

**[0013]** The separation area to which the effluent stream from the hydroconversion area is sent, whether it be in liquid or liquid/vapour phase, can include one or more atmospheric and/or vacuum distillation steps and/or one or more flash steps, whereby the separation is effected of the different fractions coming from the hydroconversion reaction from the distillation residue or from the liquid coming from the sole or last flash step, which is recycled to the ebullated bed reactor (s).

**[0014]** The separation area to which the effluent stream from the hydroconversion area is sent, if in vapour phase, can include one or more high pressure separators.

**[0015]** It is generally necessary to effect a purging on the recycled stream in order to prevent the metal sulphides, produced by the demetallation effect, from accumulating at excessively high levels which could jeopardize the process processability (not only in the hydrotreating reactor but also in the column bottoms, separators, pumps and pipes). Obviously, during the purging the catalyst is also unfortunately subtracted from the reaction cycle and must therefore be continuously reintegrated accordingly.

**[0016]** The heterogeneous hydrogenation catalyst, typical of ebullated beds, consists of a carrier and an active phase. The carrier typically used is based on alumina, silica or mixtures thereof having a suitable porosity. The active phase generally consists of two components. The first, always present, is a mixture of sulphides, one of which obtained from a metal belonging to group VIB (preferably Mo) and at least one obtained from a metal belonging to group VIII (preferably Ni or Co). The metals are initially deposited on the carrier as oxides and are then transformed into sulphides to be active in the reaction. The second consists of acidic sites introduced either by suitably regulating the composition of the carrier or by adding a second phase to the carrier such as, for example, a zeolite or a clay.

**[0017]** The preferred active phase is that having as first or sole component, a mixture of sulphides of which one derives from molybdenum and one from Ni or Co.

**[0018]** The nano-dispersed hydrogenation catalyst, i.e. with a dispersion of particles having micronic and/or sub-micronic dimensions (nano-dispersion), added to the fresh feedstock in such a quantity as to guarantee a sufficient activation degree of the hydrogen in the reactor, is based on Mo or W sulphide and can be formed in-situ starting from an

oil-soluble, decomposable precursor, or ex-situ and can possibly contain one or more transition metals.

**[0019]** The make-up of the nano-dispersed catalyst is effected together with the feed of the fresh feedstock, in order to reintegrate the nano-dispersed catalyst discharged with the purging.

**[0020]** The presence of an optimal concentration of the nano-dispersed catalyst, in addition to limiting the formation of resins or pitches, allows a better build-up of solids (determined through the HFT technique) and limits the deterioration of the supported, heterogeneous catalyst. In this way it is possible to benefit from a higher cracking activity and, at the same time, allow the recycling of the heaviest fractions to the reactor, thus avoiding the production of fuel oil. The heterogeneous supported catalyst is collected in the central section of the hydrocracking reactor, as in traditional ebullated-beds, whereas the nano-dispersed catalyst based on Mo or W sulphide, circulates with the liquid through the various sections of the plant and is recycled to the reactor. The solution allows a very high conversion to be obtained together with a better quality of the products with respect to both ebullated-bed reactors and slurry reactors.

**[0021]** This option allows all the synergies between the two technologies (ebullated-bed and slurry systems) to be fully exploited, thus providing a new and enhanced process which makes use of the positive aspects of the supported heterogeneous catalyst, typical of the ebullated-bed technology, and those of the nano-dispersed catalyst typical of the slurry technology.

**[0022]** It is also possible to use the process according to the present invention for the revamping of an existing ebullated bed plant using the existing equipment and only effecting modifications for the introduction of the dispersed, additional catalyst, separating the products and recycling the heaviest products to the hydrocracking reactor.

**[0023]** The ebullated-bed system can be carried out according to the procedure and conditions typical of the known art (see, for example, "Oil & Gas Science and Technology, Rev. IFP, Vol. 55, 2000, Nr. 4, p. 397").

**[0024]** The concentration of the transition metal in the nano-dispersed catalyst, in the feedstock, including the recycled stream, fed to the hydroconversion area, ranges from 10 to 30,000 ppm, preferably from 1,000 to 20,000 ppm.

**[0025]** The reactor(s) used is preferably run under a hydrogen pressure, or a mixture of hydrogen and hydrogen sulphide, ranging from 100 to 200 atmospheres, within a temperature range of 360 to 480° C. The mixture of gas, consisting of hydrogen and recycled gas, enters the reactor from above and is distributed through the catalytic bed by means of a suitable distributor of a specific design (grid plate).

**[0026]** The degree of purging required depends on the rate at which coke and metal sulphides are produced and on the concentration of solid matter in the reaction medium at the stationary state. By operating according to the process described, the purging to be effected can be maintained at a level lower than 10% with respect to the feedstock fed.

**[0027]** The possible distillation steps of the separation section to which the effluent stream from the hydroconversion zone is sent, can be carried out at reduced pressure, preferably between 0.001 and 0.5 MPa, more preferably between 0.01 and 0.3 MPa.

**[0028]** A preferred embodiment of the present invention is now provided with the help of FIG. 1 which, however, should not be considered a limitation of the scope of the claim itself.



[0029] The fresh heavy feedstock (1) is mixed with the fresh catalyst (2) and sent (3) to an ebullated-bed hydroconversion reactor (E) in which a supported heterogeneous catalyst is present.

[0030] A stream (4), containing the reaction product and the nano-dispersed catalyst, leaves said reactor (E) and is sent to a separation column (S) in order to separate the products (5) from the liquid fraction containing the nano-dispersed catalyst (6) which is recycled (7), after a purging (8), to the hydroconversion reactor.

### Example 1

[0031] Experimental tests were carried out in a pilot plant as represented in FIG. 1. The ebullated bed reactors were operated in a typical set of operating conditions.

Three comparative tests were conducted in the pilot plant:

[0032] test A: the heavy bottom stream from the vacuum distillation column was recycled to the reactor and only a slurry catalyst was used. No other catalysts were used during the test.

[0033] test B: the heavy bottom stream from the vacuum distillation column was recycled to the reactor and two catalysts were used: a slurry catalyst and a commercial catalyst in the ebullated beds.

[0034] test C: the heavy bottom stream from the vacuum distillation column was recycled to the reactor and only a commercial catalyst was used in the ebullated beds.

The vacuum residue feed used for the experimental tests was produced from the Basrah Light oil. The feed characterization is reported in the table 1.

TABLE 1

characterization of the VR Basrah Light		
Carbon	wt %	83.45
Hydrogen	wt %	10.07
Nitrogen	wt %	0.38
Sulfur	wt %	4.82
Asf C5	wt %	16.5
MCRT	wt %	24.77
THFi	wt %	<0.1
Mo	wppm	1795
Nichel	wppm	45
Vanadium	wppm	153
Density at 15° C.	Kg/m3	1031.4
5%	° C.	524
10%	° C.	540
20%	° C.	562
30%	° C.	581
40%	° C.	598
50%	° C.	615.5
60%	° C.	634
70%	° C.	653
80%	° C.	674.5
90%	° C.	698.5
95%	° C.	711.5

Operating conditions, products yield and HDx performances (HDS, HDN) are reported in table 2.

TABLE 2

operating conditions, products yield and HDx per-formance			
	test A	test B	Test C
Operating Conditions			
Temperature, ° C.	430	400	400
Total Pressure, barg	140	140	140
WHSV, h <sup>-1</sup> (1)	—	0.51	0.49
Mean Residence Time, h	4.3	3.9	4.1
Mo Concentration (2)	1000	1000	—
Days On Stream	30	30	6 (3)
Products distribution (wt %)			
H2S	4.0	3.7	(4)
C1-C4	8.9	9.6	(4)
PI-170° C.	9.3	6.9	(4)
170-350° C.	33.6	44.3	(4)
350-500° C.	44.1	35.5	(4)
HDN	30.0	56.3	(4)
HDS	74.0	88.0	(4)

(1) Based on the ebullated bed catalyst load

(2) Concentration in the liquid feed to the reactors

(3) Test stopped due to the ebullated bed catalyst deactivation

(4) Products yield not determined for ebullated bed catalyst continuous deactivation

[0035] Data produced in test B, using the slurry catalyst and the commercial catalyst in the ebullated bed, shows a much higher hydro-denitrogenation (HDN) and a higher hydrodesulfurization (HDS) compared to the results from test A, obtained using only the slurry catalyst. Furthermore, in test B was obtained a products yield distribution similar to that of test A, and with higher atmospheric diesel cut, but at lower operating condition severity, i.e. at a reactor temperature 30° C. lower.

1. A process for the hydroconversion of heavy oils, selected from crude oils, heavy crude oils, bitumens from tar sands, distillation residues, distillation heavy cuts, distillation deasphalting residues, vegetable oils, oils from coal and oil shale, oils from the thermo-decomposition of waste material, polymers, biomasses, comprising sending the heavy oil to a hydroconversion area, effected in one or more ebullated-bed reactors, wherein hydrogen is introduced, in the presence of a suitable heterogeneous, supported hydroconversion catalyst, and also a suitable hydrogenation catalyst, nano-dispersed in said heavy oil, and sending the stream coming from the hydroconversion area to a separation area, in which the liquid fraction separated, containing the nano-dispersed catalyst, is recycled to the ebullated-bed reactor(s).

2. The process according to claim 1, wherein the separation area to which the effluent stream from the hydroconversion area is sent, if it is in liquid or mixed liquid/vapour phase, comprises one or more atmospheric and/or vacuum distillation and/or one or more flash steps, whereby the separation is effected of the different fractions coming from the hydroconversion reaction, from the distillation residue or from the liquid leaving the sole or last flash step, which is recycled to reactor(s).

3. The process according to claim 1, wherein the separation area to which the effluent stream from the hydroconversion area is sent, if it is in vapour phase, comprises one or more high-pressure separators.

4. The process according to claim 1, wherein a purging is effected on the liquid fraction separated containing the nano-dispersed catalyst, recycled to the ebullated-bed reactor(s).

**5.** The process according to claim **1**, wherein the nano-dispersed hydrogenation catalyst is based on Mo or W sulphide.

**6.** The process according to claim **5**, wherein the nano-dispersed hydrogenation catalyst can be formed in-situ starting from a decomposable oil-soluble precursor, or ex-situ.

**7.** The process according to claim **5**, wherein the nano-dispersed hydrogenation catalyst additionally contains one or more other transition metals.

**8.** The process according to claim **5**, wherein the concentration of the hydrogenation catalyst, nano-dispersed in the feedstock, comprising the recycled stream, fed to the hydro-conversion area, defined on the basis of the concentration of metal(s) present, ranges from 10 to 30,000 ppm.

**9.** The process according to claim **8**, wherein the concentration of the hydrogenation catalyst, nano-dispersed in the feedstock, comprising the recycled stream, fed to the hydro-conversion area, ranges from 3,000 to 20,000 ppm.

**10.** The process according to claim **1**, wherein the supported heterogeneous hydrogenation catalyst is made up of a carrier and an active phase consisting of a mixture of sulphides, one of which deriving from a metal belonging to group VIB and at least one deriving from a metal belonging to group VIII.

**11.** The process according to claim **10**, wherein the metal belonging to group VIB is molybdenum.

**12.** The process according to claim **10**, wherein the metal belonging to group VIII is selected from Ni and Co.

**13.** The process according to claim **10**, wherein the active phase consists of a mixture of sulphides, one of which deriving from molybdenum and one deriving from Ni or Co.

**14.** The process according to claim **10** or **13**, wherein the active phase also consists of acidic sites introduced by either suitably regulating the composition of the carrier or by adding a second phase to the carrier.

**15.** The process according to claim **1**, wherein the hydro-conversion reactions in ebullated beds take place at temperatures ranging from 360 to 480° C. and pressures ranging from 100 to 200 atmospheres.

**16.** The process according to claim **2**, wherein the distillation steps are carried out at reduced pressure ranging from 0.001 to 0.5 MPa.

**17.** The process according to claim **17**, wherein the distillation steps are carried out at reduced pressure ranging from 0.01 to 0.3 MPa.

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