

HYDROCONVERSION OF A HYDROCARBON-BASED HEAVY FEEDSTOCK IN A HYBRID EBULLATED-ENTRAINED BED, COMPRISING PREMIXING SAID FEEDSTOCK WITH AN ORGANIC ADDITIVE

Technical field

5 The present invention relates to a process for converting heavy oil feedstocks in the presence of hydrogen, a catalyst system comprising a porous supported catalyst and a colloidal or molecular catalyst, and an organic additive.

In particular, the present invention relates to a process for hydroconversion of heavy oil feedstocks containing a fraction of at least 50% by weight having a boiling point of at least 300°C, and especially
10 heavy oil feedstocks including a significant quantity of asphaltenes and/or fractions boiling above 500°C, such as crude oils or heavy hydrocarbon fractions resulting from the atmospheric and/or vacuum distillation of a crude oil, to yield lower boiling, higher quality materials.

The process specifically comprises premixing said feedstock with an organic additive, before being brought into contact with the catalysts, these catalysts operating in one or several hybrid ebullated
15 bed reactors, in order to allow upgrading of said low-quality feedstock while minimizing fouling in equipment prior to hydroconversion in the hybrid ebullated bed reactor(s).

Prior art

Converting heavy oil feedstocks into useful end products requires extensive processing, including reducing the boiling point of the heavy oil, increasing the hydrogen-to-carbon ratio, and removing
20 impurities such as metals, sulfur, nitrogen and high carbon content compounds.

Catalytic hydroconversion is commonly used for the heavy oil feedstocks and is generally carried out using three-phase reactors in which the feedstock is brought into contact with hydrogen and a catalyst. In the reactor, the catalyst can be used in the form of a fixed bed, a moving bed, an ebullated bed or an entrained bed, as for example described in chapter 18 "Catalytic Hydrotreatment
25 and Hydroconversion: Fixed Bed, Moving Bed, Ebullated Bed and Entrained Bed" of the book "Heavy Crude Oils: From Geology to Upgrading, An Overview", published by Éditions Technip in 2011. In the case of an ebullated bed or an entrained bed, the reactor comprises an upflow of liquid and of gas. The choice of the technology generally depends on the nature of the feedstock to process, and in particular its metal content, its tolerance for impurities and the conversion targeted.

30 Some heavy feedstock hydroconversion processes are based on hybrid technologies mixing the use of different catalyst bed types, for example hybrid processes using ebullated bed and entrained bed technologies, or fixed bed and entrained bed technologies, thus generally taking advantage of each technology.

For example, it is known from the art to use contemporarily in a same hydroconversion reactor a
35 supported catalyst maintained in the ebullated bed in the reactor and an entrained catalyst of smaller size, also commonly known as a "slurry" catalyst, which is entrained out of the reactor with the effluents. This entrainment of the second catalyst is in particular enabled by a suitable density and a suitable particle size of the slurry catalyst. Hence a "hybrid ebullated-entrained bed" process, also herein called "hybrid ebullated bed" or simply "hybrid bed" process, is defined in the present
40 description as referring to the implementation of an ebullated bed comprising an entrained catalyst

in addition to a supported catalyst maintained in the ebullated bed, which can be seen as a hybrid operation of an ebullated bed and an entrained bed. The hybrid bed is in a certain sense a mixed bed of two types of catalysts of necessarily different particle size and/or density, one type of catalyst being maintained in the reactor and the other type of catalyst, the slurry catalyst, being entrained out of the reactor with the effluents.

Such a hybrid bed hydroconversion process is known to improve the traditional ebullated bed process, in particular as the addition of a slurry catalyst reduces the formation of sediments and coke precursors in the hydroconversion reactor system.

Indeed, it is known that during operation of an ebullated bed reactor for upgrading a heavy oil, the heavy oil is heated to a temperature at which the high boiling fractions of the heavy oil feedstock typically having a high molecular weight and/or low hydrogen/carbon ratio, an example of which is a class of complex compounds collectively referred to as "asphaltenes", tend to undergo thermal cracking to form free radicals of reduced chain length. These free radicals have the potential of reacting with other free radicals, or with other molecules, to produce coke precursors and sediments. A slurry catalyst passing through the reactor, while the reactor already comprises a supported catalyst maintained in the reactor, provides an additional catalytic hydrogenation activity, especially in zones of the reactor generally free of supported catalyst. The slurry catalyst hence reacts with the free radicals in these zones, forming stable molecules, and thus contributes to control and reduce the formation of sediments and coke precursors. As formation of coke and sediments is a major cause of conventional catalyst deactivation and hydroconversion equipment fouling, such a hybrid process allows increasing the lifespan of the supported catalyst and prevents the fouling of downstream equipment, such as separation vessels, distillation columns, heat exchangers etc.

For example, PCT application WO2012/088025 describes such a hybrid process for upgrading heavy feedstocks using the ebullated bed technology and a catalytic system comprising of a supported catalyst and a slurry catalyst. The ebullated bed reactor comprises the two types of catalysts having different characteristics, the first catalyst having a size greater than 0.65 mm and occupying an expanded zone, and the second catalyst having an average size of 1-300 μm and being used in suspension. The second catalyst is introduced into the ebullated bed with the feed and passes through the reactor from bottom to top. It is prepared either from unsupported bulk catalysts or by crushing supported catalysts (grain size between 1 and 300 μm).

Patent document US2005/0241991 also relates to such a hybrid bed hydroconversion process for heavy oils, and discloses one or more ebullated bed reactors, which can operate in hybrid mode with the addition of a dispersed organosoluble metal precursor in the feedstock. The addition of the catalyst precursor, which can be pre-diluted in vacuum gas oil (VGO), is carried out in an intimate mixing stage with the feedstock for preparing a conditioned feedstock prior to its introduction into the first or subsequent ebullated bed reactors. It is specified that the catalyst precursor, typically molybdenum 2-ethylhexanoate, forms a colloidal or molecular catalyst (e.g. dispersed molybdenum sulfide) once heated, by reaction with H_2S from the hydrodesulfurization of the feedstock. Such a process inhibits the formation of coke precursors and sediments that might otherwise deactivate the supported catalyst and foul the ebullated bed reactor and downstream equipment.

European patent application EP3723903 from the Applicant also discloses a hybrid bed hydroconversion process for heavy oils, wherein the dispersed solid catalyst is obtained from at least one salt of a heteropolyanion combining molybdenum and at least one metal selected from cobalt

and nickel in a Strandberg, Keggin, lacunary Keggin or substituted lacunary Keggin structure, improving hydrodeasphalting and leading to the reduction in the formation of sediments.

Slurry catalysts for heavy oil hydroconversion, and in particular colloidal or molecular catalysts formed by the use of soluble catalytic precursor, are well known in the art. It is known in particular that certain metal compounds, such as organosoluble compounds (e.g. molybdenum naphthenate or molybdenum octoate as cited in US4244839, US2005/0241991, US2014/0027344) or water-soluble compounds (e.g. phosphomolybdic acid cited in patents US3231488, US4637870 and US4637871; ammonium heptamolybdate cited in patent US6043182, salts of a heteropolyanion as cited in FR3074699), can be used as dispersed catalyst precursors and form catalysts. In case of water-soluble compounds, the dispersed catalyst precursor is generally mixed with the feedstock to form an emulsion. The dissolving of the dispersed catalyst (in general molybdenum) precursor, optionally promoted by cobalt or nickel in acid medium (in the presence of H_3PO_4) or basic medium (in the presence of NH_4OH), has been the subject of many studies and patents.

In addition to fouling due to coke precursors and sediments that can occur in the hybrid bed reactor and downstream equipment, the inventors have observed that fouling can also occur in equipment upstream, as soon as the heavy oil feedstock containing the catalyst precursor is heated before its introduction into the hydroconversion reactor.

Such a fouling in equipment upstream of the hydroconversion reactor, especially in the heating equipment of the heavy oil feedstock mixed with the catalyst precursor of the particular colloidal or molecular catalyst, seems to be mainly related to metal and carbon build-up on walls, and can limit equipment operability.

Thus, although the slurry catalyst in known hybrid processes such as those cited above is known to reduce fouling due to coke precursors and sediments in the hydroconversion reactor and downstream equipment, fouling observed in upstream equipment containing the heavy oil feedstock mixed with the catalyst precursor, such as in a preheating device, constitutes another operational issue not solved so far. Also, it has been observed that fouling due to coke precursors and sediments can still occur in downstream equipment in some cases, showing that the performance of the addition of a slurry catalyst can still be improved.

Objectives and summary of the invention

Within the context described above, an aim of the present invention is to provide a hybrid hydroconversion process implementing a colloidal or molecular catalyst formed by the use of soluble catalytic precursor, addressing the problem of fouling especially in equipment upstream the hydroconversion reactor, in particular in a preheating device of the feedstock prior its conversion in the hybrid hydroconversion reactor(s).

More generally, the present invention aims at providing a hybrid hydroconversion process for upgrading of heavy oil feedstocks allowing one or more of the following effects: reduced equipment fouling, more effective processing of asphaltene molecules, reduction in the formation of coke precursors and sediments, increased conversion level, enabling the reactor to process a wider range of lower quality feedstocks, elimination of catalyst-free zones in the ebullated bed reactor and downstream processing equipment, longer operation in between maintenance shut downs, more efficient use of the supported catalyst, increased throughput of heavy oil feedstock, and increased rate of production of converted products. Reducing the frequency of shutdown and startup of process vessels means less pressure and temperature cycling of process equipment, and this significantly increases the process safety and extends the useful life of expensive equipment.

Thus, in order to achieve at least one of the objectives targeted above, among others, the present invention provides, according to a first aspect, a process for the hydroconversion of a heavy oil feedstock containing a fraction of at least 50% by weight having a boiling point of at least 300°C, and containing metals and asphaltenes, comprising the following steps :

- 5 (a) preparing a first conditioned heavy oil feedstock by blending said heavy oil feedstock with an organic chemical compound comprising at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function;
- (b) preparing a second conditioned heavy oil feedstock by mixing a catalyst precursor composition with the first conditioned heavy oil feedstock from step (a) in a manner such that a colloidal or
- 10 molecular catalyst is formed when it reacts with sulfur;
- (c) heating the second conditioned heavy oil feedstock from step (b) in at least one preheating device;
- d) introducing said heated second conditioned heavy oil feedstock from step (c) into at least one hybrid ebullated-entrained bed reactor comprising a hydroconversion porous supported catalyst and
- 15 operating said hybrid ebullated-entrained bed reactor in the presence of hydrogen and at hydroconversion conditions to produce an upgraded material, and wherein the colloidal or molecular catalyst is formed in situ within the second conditioned heavy oil feedstock at step (c) and/or at step (d).

According to one or more embodiments, step (a) comprises mixing said organic chemical compound and said heavy oil feedstock in a dedicated vessel of an active mixing device.

According to one or more embodiments, step (a) comprises injecting said organic chemical compound into a pipe conveying said heavy oil feedstock toward the hybrid ebullated-entrained bed reactor.

According to one or more embodiments, step (a) is carried out at a temperature between room

25 temperature and 300°C, preferably between 70°C and 200°C, and the residence time of the organic chemical compound with said heavy oil feedstock before step (b) is between 1 second and 10 hours.

According to one or more embodiments, the organic chemical compound is selected from the group consisting of 2-ethylhexanoic acid, naphthenic acid, caprylic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, ethyl octanoate, ethyl 2-ethylhexanoate, 2-ethylhexyl 2-

30 ethylhexanoate, benzyl 2-ethylhexanoate, diethyl adipate, dimethyl adipate, bis(2-ethylhexyl) adipate, dimethyl pimelate, dimethyl suberate, monomethyl suberate, hexanoic anhydride, caprylic anhydride, and a mixture thereof.

According to one or more embodiments, the organic chemical compound comprises 2-ethylhexanoic acid, and preferably is 2-ethylhexanoic acid.

35 According to one or more embodiments, the organic chemical compound comprises ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate, and is preferably ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate.

According to one or more embodiments, the catalyst precursor composition comprises an oil soluble organo-metallic or bimetallic compound or complex, preferably an oil soluble organo-metallic

40 compound or complex selected from the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate, vanadium naphthanate, vanadium octoate, molybdenum hexacarbonyl, vanadium hexacarbonyl, and iron pentacarbonyl, and is preferably molybdenum 2-ethylhexanoate.

According to one or more embodiments, the molar ratio between said organic chemical compound added at step a) and the active metal(s), preferably molybdenum, of the catalyst precursor

composition added at step (b), in said second conditioned heavy oil feedstock is comprised between 0.1:1 and 20:1.

According to one or more embodiments, the colloidal or molecular catalyst comprises molybdenum disulfide.

5 According to one or more embodiments, step (b) comprises (b1) pre-mixing the catalyst precursor composition with a hydrocarbon oil diluent at a temperature below a temperature at which a substantial portion of the catalyst precursor composition begins to thermally decompose in order to form a diluted precursor mixture; and (b2) mixing said diluted precursor mixture with the first conditioned heavy oil feedstock.

10 According to one or more embodiments, step (b1) is carried out at a temperature between room temperature and 300°C and for a period of time from 1 second to 30 minutes, and step (b2) is carried out at a temperature comprised between room temperature and 300°C and for a period of time from 1 second to 30 minutes.

15 According to one or more embodiments, step (c) comprises heating at a temperature between 280°C and 450°C, more preferably between 300°C and 400°C, and most preferably between 320°C and 365°C.

20 According to one or more embodiments, the heavy oil feedstock comprises at least one of the following feedstocks : heavy crude oil, oil sand bitumen, atmospheric tower bottoms, vacuum tower bottoms, resid, visbreaker bottoms, coal tar, heavy oil from oil shale, liquefied coal, heavy bio oils, and heavy oils comprising plastic waste and/or a plastic pyrolysis oil.

25 According to one or more embodiments, the heavy oil feedstock has a sulfur at a content of greater than 0.5% by weight, a Conradson carbon residue of at least 0.5% by weight, C_7 asphaltenes at a content of greater than 1% by weight, transition and/or post-transition and/or metalloid metals at a content of greater than 2 ppm by weight, and alkali and/or alkaline earth metals at a content of greater than 2 ppm by weight.

30 According to one or more embodiments, hydroconversion step (d) is carried out under an absolute pressure of between 2 MPa and 38 MPa, at a temperature of between 300°C and 550°C, at an liquid hourly space velocity LHSV relative to the volume of each hybrid reactor of between 0.05 h^{-1} and 10 h^{-1} and under an amount of hydrogen mixed with the feedstock entering hybrid bed reactor of between 50 and 5000 Nm^3/m^3 of feedstock.

According to one or more embodiments, the concentration of the metal of the catalyst, preferably molybdenum, in the second conditioned oil feedstock is in a range of 5 ppm to 500 ppm by weight of the heavy oil feedstock.

35 According to one or more embodiments, the process comprises a step (e) of further processing the upgraded material, said step (e) comprising:

40 - a second hydroconversion step in a second hybrid ebullated-entrained bed reactor of at least a portion or all of the upgraded material resulting from the hydroconversion step (d) or optionally of a liquid heavy fraction that boils predominantly at a temperature greater than or equal to 350°C resulting from an optional separation step separating a portion or all of the upgraded material resulting from the hydroconversion step (d), said second hybrid ebullated-entrained bed reactor comprising a second porous supported catalyst and operating in the presence of hydrogen and at hydroconversion conditions to produce a hydroconverted liquid effluent with a reduced Conradson carbon residue, and possibly a reduced quantity of sulfur, and/or nitrogen, and/or metals,
- a step of fractionating a portion or all of said hydroconverted liquid effluent in a fractionation

section to produce at least one heavy cut that boils predominantly at a temperature greater than or equal to 350°C, said heavy cut containing a residual fraction that boils at a temperature greater than or equal to 540°C;

- an optional step of deasphalting, in a deasphalter, of a portion or all of said heavy cut with at least one hydrocarbon solvent to produce a deasphalted oil DAO and a residual asphalt; and

wherein, said hydroconversion step (d) and said second hydroconversion step are carried out under an absolute pressure of between 2 and 38 MPa, at a temperature of between 300°C and 550°C, at a liquid hourly space velocity LHSV relative to the volume of each hybrid ebullated-entrained bed reactor of between 0.05 h⁻¹ and 10 h⁻¹ and under an amount of hydrogen mixed with the feedstock entering each hybrid ebullated-entrained bed reactor of between 50 and 5000 Nm³/m³ of feedstock.

Other subjects and advantages of the invention will become apparent on reading the description which follows of specific exemplary embodiments of the invention, given by way of non-limiting examples, the description being made with reference to the appended figures described below.

List of the figures

Figure 1 is a block diagram illustrating the principle of the hybrid bed hydroconversion process according to the invention.

Figure 2 is a block diagram illustrating an example of a hybrid bed hydroconversion process and system according to the invention.

Figure 3 is a graph showing the fouling tendency of examples of conditioned oil feedstocks as prepared in the hybrid bed hydroconversion process according to the invention and according to prior art.

Description of the embodiments

The object of the invention is to provide hybrid bed hydroconversion methods and systems for improving the quality of a heavy oil feedstock.

Such methods and systems for hydroconverting heavy oil feedstocks employ a dual catalyst system that includes a molecular or colloidal catalyst dispersed within the heavy oil feedstock and a porous supported catalyst. They also employ an organic additive mixed with the heavy oil feedstock, prior to operating the dual catalyst system in one or more ebullated bed reactors, each of which comprising a solid phase comprising an expanded bed of a porous supported catalyst, a liquid hydrocarbon phase comprising the heavy oil feedstock, the colloidal or molecular catalyst dispersed therein and the organic additive, and a gaseous phase comprising hydrogen gas.

The hybrid bed hydroconversion methods and systems of the invention reduce equipment fouling, and especially fouling in equipment upstream the hydroconversion reactor(s), in particular in preheating equipment of the feedstock prior its conversion in the hybrid hydroconversion reactor(s), and can effectively process asphaltenes, reduce or eliminate the formation of coke precursors and sediments, increase conversion level especially by allowing hydroconversion to be operated at high temperature, and eliminate catalyst-free zones that would otherwise exist in conventional ebullated bed hydroconversion reactor(s) and downstream processing equipment. The hybrid bed hydroconversion methods and systems of the invention also allows more efficient usage of the porous supported catalyst, and of the combined dual catalyst system.

Terminology

Some definitions are given below, although more details on the objects hereafter defined shall be given further in the description.

The term "hydroconversion" shall refer to a process whose primary purpose is to reduce the boiling range of a heavy oil feedstock and in which a substantial portion of the feedstock is converted into products with boiling ranges lower than that of the original feedstock. Hydroconversion generally involves fragmentation of larger hydrocarbon molecules into smaller molecular fragments having a fewer number of carbon atoms and a higher hydrogen-to-carbon ratio. Reactions implemented during hydroconversion allow the size of hydrocarbon molecules to be reduced, mainly by cleavage of carbon-carbon bonds, in the presence of hydrogen in order to saturate the cut bonds and aromatic rings. The mechanism by which hydroconversion occurs typically involves the formation of hydrocarbon free radicals during fragmentation mainly by thermal cracking, followed by the capping of the free radical ends or moieties with hydrogen in the presence of active catalyst sites. Of course, during a hydroconversion process other reactions typically associated with "hydrotreating" can occur such as the removal of sulfur and nitrogen from the feedstock as well as olefin saturation.

The term "hydrocracking" is often used as a synonym for "hydroconversion" according to the English terminology, although "hydrocracking" shall rather refer to a process similar to hydroconversion but in which cracking of hydrocarbon molecules is mainly a catalytic cracking, that is a cracking occurring in the presence of a hydrocracking catalyst having a phase responsible for the cracking activity, for example acidic sites as for example contained in clay or zeolites. According to the French terminology for example, hydrocracking which can be translated as "hydrocraquage" generally refers to this last definition (catalytic cracking), and its usage is for example rather reserved for the case of vacuum distillates as oil feedstocks to be converted, whereas the French term "hydroconversion" is generally reserved for the conversion of heavy oils feedstocks like atmospheric and vacuum residues (but not only).

The term "hydrotreating" shall refer to a milder operation whose primary purpose is to remove impurities such as sulfur, nitrogen, oxygen, halides, and trace metals from the feedstock and saturate olefins and/or stabilize hydrocarbon free radicals by reacting them with hydrogen rather than allowing them to react with themselves. The primary purpose is not to change the boiling range of the feedstock. Hydrotreating is most often carried out using a fixed bed reactor, although other hydroprocessing reactors can also be used for hydrotreating, an example of which is an ebullated bed hydrotreatment reactor.

The term "hydroprocessing" shall broadly refer to both "hydroconversion"/"hydrocracking" and "hydrotreating" processes.

The term "hydroconversion reactor" shall refer to any vessel in which hydroconversion of a feedstock is the primary purpose, e.g. the cracking of the feed (i.e. reducing the boiling range), in the presence of hydrogen and a hydroconversion catalyst. Hydroconversion reactors typically comprise an input port into which a heavy oil feedstock and hydrogen can be introduced, and an output port from which an upgraded material can be withdrawn. Specifically, hydroconversion reactors are also characterized by having sufficient thermal energy to cause fragmentation of larger hydrocarbon molecules into smaller molecules by thermal decomposition. Examples of hydroconversion reactors include, but are not limited to, slurry bed reactors, also known as entrained bed reactors (three phase – liquid, gas, solid – reactors, wherein the solid and liquid phases can behave like a homogeneous phase), ebullated bed reactors (three phase fluidized reactors), moving bed reactors (three phase reactors with downward movement of the solid catalyst and upward or downward flow of liquid and gas), and fixed bed reactors (three phase reactors with liquid feed trickling downward over a fixed bed of solid supported catalyst with hydrogen typically flowing concurrently with the liquid, but possibly countercurrently in some cases).

The terms “hybrid bed” and “hybrid ebullated bed” and “hybrid entrained-ebullated bed” for a hydroconversion reactor shall refer to an ebullated bed hydroconversion reactor comprising an entrained catalyst in addition to a porous supported catalyst maintained into the ebullated bed reactor. Similarly, for a hydroconversion process, these terms shall thus refer to a process comprising a hybrid operation of an ebullated bed and an entrained bed in at least a same hydroconversion reactor. The hybrid bed is a mixed bed of two type of catalysts of necessarily different particle size and/or density, one type of catalyst – the “porous supported catalyst” - being maintained in the reactor and the other type of catalyst – the entrained catalyst”, also commonly referred as “slurry catalyst” - being entrained out of the reactor with the effluents (upgraded feedstock). In the present invention, the entrained catalyst is a colloidal catalyst or molecular catalyst, as defined below.

The terms "colloidal catalyst" and "colloidally dispersed catalyst" shall refer to catalyst particles having a particle size that is colloidal in size, e.g. less than 1 µm in size (diameter), preferably less than 500 nm in size, more preferably less than 250 nm in size, or less than 100 nm in size, or less than 50 nm in size, or less than 25 nm in size, or less than 10 nm in size, or less than 5 nm in size. The term "colloidal catalyst" includes, but is not limited to, molecular or molecularly-dispersed catalyst compounds.

The terms "molecular catalyst" and "molecularly dispersed catalyst" shall refer to catalyst compounds that are essentially "dissolved" or completely dissociated from other catalyst compounds or molecules in a heavy oil hydrocarbon feedstock, non-volatile liquid fraction, bottoms fraction, resid, or other feedstock or product in which the catalyst may be found. It shall also refer to very small catalyst particles or slabs that only contain a few catalyst molecules joined together (e.g. 15 molecules or less).

The terms "porous supported catalyst", "solid supported catalyst", and "supported catalyst" shall refer to catalysts that are typically used in conventional ebullated bed and fixed bed hydroconversion systems, including catalysts designed primarily for hydrocracking or hydrodemetallization and catalysts designed primarily for hydrotreating. Such catalysts typically comprise (i) a catalyst support having a large surface area and numerous interconnected channels or pores and (ii) fine particles of an active catalyst such as sulfides of cobalt, nickel, tungsten, and/or molybdenum dispersed within the pores. Supported catalysts are commonly produced as cylindrical pellets or spherical solids, although other shapes are possible.

The terms "upgrade", "upgrading" and "upgraded", when used to describe a feedstock that is being or has been subjected to hydroconversion, or a resulting material or product, shall refer to one or more from among: a reduction in the molecular weight of the feedstock, a reduction in the boiling point range of the feedstock, a reduction in the concentration of asphaltenes, a reduction in the concentration of hydrocarbon free radicals, a reduction of Conradson carbon residue, an increase of H/C atomic ratio of the feedstock, and a reduction in the quantity of impurities, such as sulfur, nitrogen, oxygen, halides, and metals.

The terms "conditioned feedstock" and “conditioned heavy oil feedstock” shall refer to the heavy oil feedstock to be treated into at least a hydroconversion hybrid bed reactor, feedstock in which an organic additive has been combined (here “first conditioned feedstock”), or into which such an organic additive has been combined and then a catalyst precursor composition has been combined and mixed sufficiently so that, upon formation of the catalyst, especially by reaction with sulfur, the catalyst will comprise a colloidal or molecular catalyst dispersed within the feedstock (here “second conditioned feedstock”).

In what follows, the term “comprise” is synonymous with (means the same thing as) “include” and “contain” and is inclusive or open and does not exclude other unspecified elements. It will be understood that the term “comprise” includes the exclusive and closed term “consist”.

The terms “comprised between ... and ...” and “in the ... to ... range” and “in a range of ... to ...” mean that the values at the limits of the interval are included in the range of values described, unless specified otherwise.

In the detailed description below, numerous specific details are set out in order to convey a deeper understanding of the process and system according to the invention. However, it will be apparent to the skilled person that the process and system can be employed without all these specific details. In other cases, characteristics which are well known have not been described in detail, in order not to complicate the description to no purpose.

Figure 1 is a block diagram schematically illustrating the principle of the hybrid bed hydroconversion process 100 according to the invention. It differs in particular from a conventional hybrid bed process as disclosed for example in US2005/0241991 in that it comprises the addition of an organic additive to the feedstock prior its mixing with a catalyst precursor composition.

The terms “organic chemical compound” and “organic additive” are indifferently used in the present description to designate the chemical compound comprising at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function added to the heavy oil feedstock at step (a) and described in detail further below.

According to the invention, a heavy oil feedstock 101 containing a fraction of at least 50% by weight having a boiling point of at least 300°C, and containing metals and asphaltenes, is treated in a hydroconversion process 100 comprising the following steps:

(a) preparing a first conditioned heavy oil feedstock 103 by blending said heavy oil feedstock 101 with an organic chemical compound 102 comprising at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function;

(b) preparing a second conditioned heavy oil feedstock 105 by mixing a catalyst precursor composition 104 with the first conditioned heavy oil feedstock 103 from step (a) in a manner so that a colloidal or molecular catalyst is formed when it reacts with sulfur;

(c) heating the second conditioned heavy oil feedstock from step (b) in at least one preheating device;

(d) introducing the heated second conditioned heavy oil feedstock 106 from step (c) into at least one hybrid ebullated-entrained bed reactor comprising a hydroconversion porous supported catalyst and operating said hybrid ebullated-entrained bed reactor in the presence of hydrogen and at hydroconversion conditions to produce an upgraded material 107.

The upgraded material 107 can be further processed in optional step (e).

In the hydroconversion process according to the invention, the colloidal or molecular catalyst is formed in situ within the second conditioned heavy oil feedstock at step (c) and/or at step (d).

Each step, stream and material involved are now detailed below.

Some of the numerical references mentioned below relate to figure 2, which illustrates schematically an example of a hybrid bed hydroconversion system 200 according to the invention, said system being described in detail later in the description, after the description of the general process.

Heavy oil feedstock

The term "heavy oil feedstock" shall refer to heavy crude oils, oil sand bitumen, bottom of the barrel and resid left over from refinery processes (e.g. visbreaker bottoms), and any other lower quality material that contains a substantial quantity of high boiling hydrocarbon fractions and/or that includes a significant quantity of asphaltenes that can deactivate a solid supported catalyst and/or cause or result in the formation of coke precursors and sediments.

The heavy oil feedstock 101 can thus comprise at least one of the following feedstocks: heavy crude oil, oil sand bitumen, atmospheric tower bottoms, vacuum tower bottoms, resid, visbreaker bottoms, coal tar, heavy oil from oil shale, liquefied coal, heavy bio oils, and heavy oils comprising plastic waste and/or a plastic pyrolysis oil.

Plastic pyrolysis oils are oils obtained from the pyrolysis of plastics, preferably of plastic waste, and may be obtained from a thermal, catalytic pyrolysis treatment or else may be prepared by hydropyrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

In particular, the treated heavy oil feedstock contains hydrocarbon fractions of which at least 50% by weight, preferably at least 80% by weight has a boiling temperature of at least 300°C, preferably at least 350°C or at least 375°C.

These are crude oils or heavy hydrocarbon fractions resulting from the atmospheric and/or vacuum distillation of a crude oil. They can also be atmospheric and/or vacuum residues, and in particular atmospheric and/or vacuum residues resulting from hydrotreatment, hydrocracking and/or hydroconversion. It can also be vacuum distillates, cuts from a catalytic cracking unit such as fluid catalytic cracking (FCC), a coking or visbreaking unit.

Preferably, they are vacuum residues. Generally these residues are fractions in which at least 80% by weight has a boiling temperature of at least 450°C or more, and most often at least 500°C or 540°C.

Aromatic cuts extracted from a lubricant production unit, deasphalted oils (raffinates from a deasphalting unit), and asphalt (residues from a deasphalting unit) are also suitable as feedstock.

The feedstock can also be a residual fraction from direct coal liquefaction (vacuum distillate and/or atmospheric and/or vacuum residue from e.g. H-Coal process, registered trademark), coal pyrolysis or shale oil residues, or a residual fraction from the direct liquefaction of lignocellulosic biomass alone or mixed with coal and/or a petroleum fraction (herein called "heavy bio oils").

Examples of heavy oil feedstocks include, but are not limited to, Lloydminster heavy oil, Cold Lake bitumen, Athabasca bitumen, Urals crude oil, Arabian Heavy crude oil, Arabian Light crude oil, atmospheric tower bottoms, vacuum tower bottoms, residuum (or "resid"), resid pitch, vacuum residue, solvent deasphalting pitch, and nonvolatile liquid fractions that remain after subjecting crude oil, bitumen from tar sands, liquefied coal, oil shale, or coal tar feedstocks to distillation, hot separation, and the like and that contain higher boiling fractions and/or asphaltenes.

All these feedstocks can be used alone or in a mixture.

The heavy oil feedstocks treated in the process and system according to the invention contain metals and asphaltenes, in particular C₇ asphaltenes, and other impurities such as sulfur and nitrogen. The term "asphaltene" shall refer to the fraction of a heavy oil feedstock that is typically insoluble in paraffinic solvents such as propane, butane, pentane, hexane, and heptane and that includes sheets of condensed cyclic compounds held together by hetero atoms such as sulfur, nitrogen, oxygen and metals. Asphaltenes broadly include a wide range of complex compounds having anywhere from 80

to 160,000 carbon atoms. Asphaltenes are defined operationally as “C₇ asphaltenes”, i.e. heptane-insoluble compounds according to the standard ASTM D 6560 (also corresponding to standard NF T60-115), and any content in asphaltenes refers to C₇ asphaltenes in the present description. C₇ asphaltenes are compounds known to inhibit the conversion of residual cuts, both by their ability to form heavy hydrocarbon residues, commonly known as coke, and by their tendency to produce sediments that severely limit the operability of hydrotreating and hydroconversion units.

The heavy oil feedstock 101 can typically have sulfur at a content of greater than 0.5% by weight, Conradson carbon residue of at least 3% by weight, C₇ asphaltenes at a content of greater than 1% by weight, transition and/or post-transition and/or metalloid metals at a content of greater than 2 ppm by weight, and alkali and/or alkaline earth metals at a content of greater than 2 ppm by weight.

These types of feedstocks are indeed generally rich in impurities such as metals, in particular transition metal (e.g. Ni, V) and/or post-transition metal, and/or metalloid, for which a content can be greater than 2 ppm by weight, or greater than 20 ppm by weight, and even greater than 100 ppm by weight, and also alkali metal (e.g. Na) and/or alkaline earth metal whose content can be higher than 2 ppm by weight, even higher than 5 ppm by weight, and even higher than 7 ppm by weight. The sulfur content is indeed generally higher than 0.5% by weight, and even higher than 1% by weight, or even greater than 2% by weight.

The content of C₇ asphaltenes can indeed be at least 1% by weight, and even higher than 3% by weight.

The Conradson carbon residue is indeed in general higher than 3% by weight, and even of at least 5% by weight. The Conradson carbon residue is defined by ASTM D 482 standard and represents the amount of carbon residue produced after pyrolysis under standard conditions of temperature and pressure.

These contents are expressed in % by weight of the total weight of the feed.

Step (a): preparation of the first conditioned heavy oil feedstock: heavy oil feedstock + organic additive

Step (a) comprises blending said heavy oil feedstock 101 with an organic chemical compound 102 comprising at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function. This blending forms what is referred to herein as a first conditioned heavy oil feedstock 103.

This step is implemented before step (b) of thorough/intimate mixing with a catalyst precursor composition that will lead to the formation of a colloidal or molecular catalyst dispersed within the heavy oil when it will react with sulfur.

The inventors have shown that the mixing step (a) between such an organic additive and the heavy oil feedstock, before step (b), improves the hybrid ebullated-entrained bed hydroconversion process, in particular by reducing the fouling of the equipment, especially upstream the hydroconversion reactor in the feedstock heating equipment at step c).

Without being bound by any theory, the organic additive, mixed with the heavy oil feedstock, allows a better solubility of the colloidal or molecular catalyst precursor in the feed, avoiding or reducing fouling in particular due to metal deposition in equipment upstream of the hydroconversion reactor like in the heating equipment, and improving therefore the dispersion of the colloidal or molecular catalyst formed at step c) and/or at a later stage, thus generating a greater availability of the metal

active sites, favoring the hydrogenation of free radicals which are precursors of coke and sediments, and generating a substantial reduction of the fouling of the equipment.

The organic additive

The organic additive 102 having at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function preferably comprises at least 6 carbon atoms, and more preferably at least 8 carbon atoms.

Typically, the organic additive 102 is not a catalyst precursor nor a catalyst.

In particular, the organic additive 102 does not contain any metal.

Examples of organic additive include, but are not limited to, 2-ethylhexanoic acid, naphthenic acid, caprylic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, ethyl octanoate, ethyl 2-ethylhexanoate, 2-ethylhexyl 2-ethylhexanoate, benzyl 2-ethylhexanoate, diethyl adipate, dimethyl adipate, bis(2-ethylhexyl) adipate, dimethyl pimelate, dimethyl suberate, monomethyl suberate, hexanoic anhydride, caprylic anhydride. Advantageously, the organic additive is an organic chemical compound selected from the group consisting of the list of specific compounds recited just above, and a mixture thereof.

Preferably, the organic additive is an organic chemical compound comprising at least one carboxylic acid function, and more preferably selected from the group consisting of 2-ethylhexanoic acid, naphthenic acid, caprylic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid.

More preferably, the organic additive comprises, or consists of, 2-ethylhexanoic acid.

The organic additive can be an organic chemical compound comprising at least one ester function and/or an acid anhydride function, and for example selected from the group consisting of ethyl octanoate, ethyl 2-ethylhexanoate, 2-ethylhexyl 2-ethylhexanoate, benzyl 2-ethylhexanoate, diethyl adipate, dimethyl adipate, bis(2-ethylhexyl) adipate, dimethyl pimelate, dimethyl suberate, monomethyl suberate, and/or from the group consisting of hexanoic anhydride and caprylic anhydride.

More preferably, the organic additive comprising at least one ester function and/or an acid anhydride function comprises, or consists of, ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate or a mixture thereof, and preferably is ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate.

This step (a) of mixing the organic additive 102 with the heavy oil feedstock 101 forming the first conditioned heavy oil feedstock 103 is implemented before step (b) of thorough/intimate mixing with a catalyst precursor composition that will lead to the formation of the colloidal or molecular catalyst dispersed within the heavy oil.

The organic additive is preferably added such that the molar ratio of organic additive to the active metal(s) of the catalyst precursor composition added at step (b) is in a range of about 0.1:1 to about 20:1, more preferably in a range of about 0.75:1 to about 7:1, and even more preferably in a range of about 1:1 to about 5:1. The term "about" shall refer to an approximation of $\pm 5\%$, preferably $\pm 1\%$.

Advantageously, the catalyst precursor composition added at step (b) comprises Mo, e.g. molybdenum 2-ethylhexanoate, and the organic additive is preferably added such that the molar ratio of organic additive to Mo of the catalyst precursor composition added at step (b) is in a range of about 0.1:1 to about 20:1, more preferably in a range of about 0.75:1 to about 7:1, and even more preferably in a range of about 1:1 to about 5:1.

Mixing with the organic additive

The mixing of the organic additive and of the heavy oil feedstock is advantageously carried out in a first conditioner mixer 210.

The first conditioner mixer 210 may comprise an active mixing device, any type of injection system for pipes or any type of in-line mixer as detailed below.

- 5 According to one or more embodiments, the preparation of the first conditioned heavy oil feedstock 103 comprises mixing said organic additive 102 and said heavy oil feedstock 101 in a dedicated vessel of an active mixing device (forming the first conditioner mixer 210).

The term “active mixing device” shall refer to a mixing device comprising a mobile part, e.g. a stirring rod, to actively mix the components.

- 10 Such a configuration allows in particular to increase the dispersion of the colloidal or molecular catalyst formed in a later stage. The use of a dedicated vessel also enables a long residence time.

According to one or more embodiments, the preparation of the first conditioned heavy oil feedstock 103 comprises injecting said organic chemical compound 102 into a pipe conveying said heavy oil feedstock 101 towards the hybrid ebullated-entrained bed reactor. The first conditioner mixer 210

- 15 thus comprises in such a configuration the portion of the pipe wherein the mixing is performed, and possibly additional systems to help the mixing, for example static in-line mixers as described further on in step (b).

Such a configuration can in particular reduce equipment investment and required footprint compared to mixing in a dedicated vessel.

- 20 The residence time of the organic additive with the heavy oil feedstock before mixing with the catalyst precursor composition in step (b) forming the second conditioned heavy oil feedstock 105 is preferably between 1 second and 10 hours, more preferably between 1 second and 1 hour, and even more preferably between 1 second and 30 minutes. In the present description, a mixing time (or residence time for mixing) of 1 second includes an instantaneous mixing.

- 25 The mixing of the organic additive and of the heavy oil feedstock is preferably carried out between room temperature, e.g. 15°C, and 300°C, more preferably between 70°C and 200°C, for example at 150°C.

The temperature at which the mixing is done is advantageously the actual temperature of the heavy oil feedstock stream 101.

- 30 The temperature at step (a) should be preferably lower than a decomposition temperature of the catalyst precursor composition.

The pressure for the mixing step (a) is also advantageously the actual pressure of the stream of heavy oil feedstock 101. Preferably, the gauge pressure for the mixing stage (a) is between 0 MPa and 25 MPa, more preferably between 0.01 MPa and 5 MPa.

- 35 In the case of heavy oil feedstocks which are solid or extremely viscous at room temperature, such feedstocks may advantageously be heated in order to soften them and create a feedstock having a viscosity low enough to allow good mixing of the organic additive, and notably with the catalyst precursor composition in the additional step (b). In general, the decrease in the viscosity of the heavy oil feedstock will reduce the time required for carrying out the thorough and intimate mixing of the catalyst precursor composition in the first conditioned feedstock at step (b). However, the feedstock
40 should not be heated to a temperature beyond which significant thermal decomposition of the catalyst precursor composition occurs until after thorough and complete mixing with the catalyst precursor composition at step (b). The premature thermal decomposition of the catalyst precursor

composition generally results in the formation of micron-sized or larger catalyst particles rather than a colloidal or molecular catalyst.

At step (a), the blending of the heavy oil feedstock 101 with the organic additive 102 can be done for the heavy oil feedstock 101, partly or completely.

- 5 According to one or more preferred embodiments, the mixing step (a) is carried out between the organic additive 102 and the entire stream of the heavy oil feedstock 101 sent to the hydroconversion system. According to one or more variants, the mixing step (a) is carried out between the organic additive 102 and a part of the flow of the heavy oil feedstock 101 sent to the hydroconversion. Thus preparing the first conditioned heavy oil feedstock 103 can be carried out by
- 10 blending at least one portion of the stream of said heavy oil feedstock 101, for example at least 50 wt. % of the stream of said heavy oil feedstock 101, with the organic additive 102. The complementary portion of the stream of said heavy oil feedstock 101 may be reincorporated once the catalyst precursor composition has been added (step (b)), that is to say mixed with the second conditioned heavy oil feedstock before its preheating at step (c).

15 **Step (b): preparation of the second conditioned heavy oil feedstock: mixing with the catalyst precursor composition**

The first conditioned oil feedstock 103 is then mixed with a catalyst precursor composition 104 to form a second conditioned heavy oil feedstock 105.

Catalyst precursor composition

- 20 The catalyst precursor composition is selected from all metal catalyst precursors known to a person skilled in the art, capable of forming a colloidally or molecularly dispersed catalyst (i.e. the slurry catalyst) in the presence of hydrogen and/or H₂S and/or any other source of sulfur, and enabling the hydroconversion of a heavy oil feedstock after injection into said heavy oil feedstock.

The catalyst precursor composition is advantageously an oil soluble catalyst precursor composition at least containing one transition metal.

25 The catalyst precursor composition preferably comprises an oil soluble organo-metallic compound or complex.

The catalyst precursor composition can comprise an oil soluble organo-metallic or bimetallic compound or complex comprising one or two of the following metals: Mo, Ni, V, Fe, Co or W, or

30 blends of such compounds/complexes.

The oil soluble catalyst precursor composition preferably has a decomposition temperature (temperature under which the catalyst precursor composition is substantially chemically stable) in a range from 100°C to 350°C, more preferably in a range of 150°C to 300°C, and most preferably in a range of 175°C to 250°C.

- 35 The oil soluble organo-metallic compound or complex is preferably selected from the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate, vanadium naphthanate, vanadium octoate, molybdenum hexacarbonyl, vanadium hexacarbonyl, and iron pentacarbonyl. These compounds are non-limiting examples of oil soluble catalyst precursor compositions.

More preferably the catalyst precursor composition comprises molybdenum and for example

40 comprises a compound selected in the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate, and molybdenum hexacarbonyl.

A currently preferred catalyst precursor composition comprises, or consists of, molybdenum 2-ethylhexanoate (also commonly known as molybdenum octoate). Typically, molybdenum 2-

ethylhexanoate contains 15% by weight of molybdenum and has a decomposition temperature or range high enough to avoid substantial thermal decomposition when mixed with a heavy oil feedstock at a temperature below 250°C.

- One of skill in the art can, following the present disclosure, select a mixing temperature profile that results in mixing of a selected precursor composition without substantial thermal decomposition prior to formation of the colloidal or molecular catalyst.

Mixing with the catalyst precursor composition

The mixing of the catalyst precursor composition and of the first conditioned heavy oil feedstock is carried out in a second conditioner mixer 220.

- The catalyst precursor composition 104, preferably an oil soluble catalyst precursor composition, can be pre-mixed with a diluent hydrocarbon stream to form a diluted precursor mixture, as described in US2005/0241991, US10822553 or US10941353 and recalled below.

According to one or more preferred embodiments, step (b) comprises:

- (b1) pre-mixing the catalyst precursor composition 104 with a hydrocarbon oil (diluent) to form a diluted precursor mixture, said pre-mixing being preferably carried out at a temperature below a temperature at which a substantial portion of the catalyst precursor composition begins to decompose, preferably between room temperature, e.g. 15°C, and 300°C, and advantageously for a period of time from 1 second to 30 minutes; and
- (b2) mixing said diluted precursor mixture with the first conditioned heavy oil feedstock 103, preferably at a temperature between room temperature, e.g. 15°C, and 300°C and advantageously for a period of time from 1 second to 30 minutes.

- Examples of suitable hydrocarbon diluents include, but are not limited to, vacuum gas oil known as "VGO" (which typically has a boiling range of 360°C-524°C), decant oil or cycled oil (which typically has a boiling range of 360°C-550°C), light gas oil (which typically have a boiling range of 200°C-360°C), vacuum residues (which typically has a boiling temperature of 524°C+), deasphalted oils, and resins. The hydrocarbon diluent is preferably a VGO.

The mass ratio of catalyst precursor composition 104 to hydrocarbon oil diluent is preferably in a range of about 1:500 to about 1:1, more preferably in a range of about 1:150 to about 1:2, and even more preferably in a range of about 1:100 to about 1:5 (e.g. 1:100, 1:50, 1:30, or 1:10).

- The catalyst precursor composition 104 is more preferably mixed with the hydrocarbon diluent at temperature comprised between room temperature, e.g. 15°C, and 200°C, even more preferably comprised between 50°C and 200°C, and even more preferably comprised between 75°C and 150°C, and even more preferably between 75°C and 100°C, to form the diluted precursor mixture.

- It is understood that the actual temperature at which the diluted precursor mixture is formed typically depends largely on the decomposition temperature of the specific precursor composition that is utilized.

The catalyst precursor composition 104 is more preferably mixed with the hydrocarbon oil diluent for a period of time within a range from 1 second to 10 minutes, and even more preferably within a range from 2 seconds to 3 minutes.

- The actual mixing time depends, at least in part, on the temperature (i.e., which affects the viscosity of the fluids) and on the mixing intensity. The mixing intensity depends, at least in part, on the number of stages e.g. for in-line static mixer.

Whereas it is within the scope of the invention to directly blend the catalyst precursor composition 104 with the first conditioned heavy oil feedstock, care must be taken in such cases to mix the

components for a time sufficient to thoroughly/intimately blend the catalyst precursor composition within the feedstock before forming the catalyst. However, a long mixing time, for example 24-hour mixing, can make certain industrial operations prohibitively expensive.

Pre-mixing the catalyst precursor composition 104 with a hydrocarbon diluent prior to blending the diluted precursor mixture with the heavy oil feedstock greatly aids in thoroughly and intimately blending the precursor composition within the feedstock, particularly in the relatively short period of time required for large-scale industrial operations to be economically viable.

Forming a diluted precursor mixture shortens the overall mixing time by (1) reducing or eliminating differences in solubility between the more polar catalyst precursor composition and the heavy oil feedstock, (2) reducing or eliminating differences in rheology between the catalyst precursor composition and the heavy oil feedstock, and/or (3) breaking up the catalyst precursor molecules to form a solute within a hydrocarbon oil diluent that is much more easily dispersed within the heavy oil feedstock. It is particularly advantageous to first form a diluted precursor mixture in the case where the heavy oil feedstock contains water (e.g. condensed water). Otherwise, the greater affinity of the water for the polar catalyst precursor composition can cause localized agglomeration of the catalyst precursor composition, resulting in poor dispersion and formation of micron-sized or larger catalyst particles. The hydrocarbon oil diluent is preferably substantially water free (i.e. , contains less than 0.5% by weight of water, preferably less than 0.1% by weight of water, and more preferably less than 750 ppm by weight of water) to prevent the formation of substantial quantities of micron-sized or larger catalyst particles.

The diluted precursor mixture is then combined with the first conditioned heavy oil feedstock 103 and mixed for a sufficient time and in such a way so as to disperse the catalyst precursor composition throughout the feedstock in order to yield a second conditioned heavy oil feedstock 105 wherein the catalyst precursor composition is thoroughly/intimately mixed with the heavy oil feedstock.

In order to obtain sufficient mixing of the catalyst precursor composition in the heavy oil feedstock before forming the colloidal or molecular catalyst, the diluted precursor mixture and heavy oil feedstock are more preferably mixed for a period of time within a range from 1 second to 10 minutes, and most preferably within a range from 2 seconds to 3 minutes. Increasing the vigorousness and/or shearing energy of the mixing process generally reduces the time required to effect thorough/intimate mixing.

Examples of mixing apparatus that can be used to effect thorough/intimate mixing of the catalyst precursor composition 104 and the first conditioned heavy oil feedstock 103 include, but are not limited to, high shear mixing such as mixing created in a pump with a propeller or turbine impeller; multiple static in-line mixers; multiple static in-line mixers in combination with in-line high shear mixers; multiple static in-line mixers in combination with in-line high shear mixers followed by a pump around in the surge vessel; combinations of the above devices followed by one or more multi-stage centrifugal pumps. According to one embodiment, continuous rather than batch-wise mixing can be carried out using high energy pumps having multiple chambers within which the catalyst precursor composition 104 and the first conditioned heavy oil feedstock 103 are churned and mixed as part of the pumping process itself. The foregoing mixing apparatus may also be used for the premixing stage (b1) discussed above in which the catalyst precursor composition 104 is mixed with the hydrocarbon oil diluent to form the catalyst precursor mixture.

Alternatively, the diluted precursor mixture 104 can be initially mixed with 20% of the first conditioned heavy oil feedstock, the resulting mixed first conditioned heavy oil feedstock can be

mixed in with another 40% of the first conditioned heavy oil feedstock, and the resulting 60% of the mixed first conditioned heavy oil feedstock can be mixed in with the remainder 40% of first conditioned heavy oil in accordance with good engineering practice of progressive dilution to thoroughly dispersed the catalyst precursor composition 104 in the heavy oil feedstock. Mixing time in the appropriate mixing devices or methods described herein should still be used in the progressive dilution approach.

The first conditioned heavy oil feedstock 103 and the diluted precursor mixture are preferably mixed and conditioned at a temperature in a range from 50°C to 200°C, more preferably in a range from 75°C to 175°C, to give the second conditioned oil feedstock. Preferably, the gauge pressure is between 0 MPa and 25 MPa, more preferably between 0.01 MPa and 5 MPa.

Step (c): Heating the second conditioned heavy oil feedstock

The second conditioned oil feedstock 105 formed at step (b) is then heated in at least one preheating device 230, before being introduced in the hybrid bed reactor for hydroconversion.

The second conditioned oil feedstock 105 is sent to the at least one preheating device 230 optionally pressurized by a pump.

The preheating device comprises any heating means capable of heating a heavy oil feedstock known to a person skilled in the art. The preheating device can comprise a furnace comprising at least a preheating chamber, and/or tubes in which the oil feed flows, mixer of the second conditioned oil feedstock with H₂, any type of suitable heat exchangers, for example tube or spiral heat exchangers in which the oil feed flows etc.

This pre-heating of the second conditioned heavy oil feedstock then allows a target temperature in the hydroconversion reactor to be reached at the later step (d).

The second conditioned oil feedstock 105 is more preferably heated in the preheating device 230 to a temperature in a range of 280°C to 450°C, even more preferably in a range of 300°C to 400°C, and most preferably in a range of 320°C to 365°C, in particular in order to later reach a target temperature in the hydroconversion reactor at step (d).

The skin temperature of the preheating device, e.g. skin temperature of the steel shell of a chamber or tubes of a furnace or heat exchanger(s), can reach 400°C to 650°C. The mixing of the heavy oil feedstock with the organic additive at step (a) avoids or reduces fouling that can occur in the preheating device at these high temperatures.

According to one or more embodiments, the second conditioned feedstock is heated to a temperature that is 100°C less than the hydroconversion temperature within the hybrid hydroconversion reactor, preferably 50°C less than the hydroconversion temperature. For example, for a hydroconversion temperature in the range 410°C-440°C, the conditioned oil feedstock can be heated at step (c) at a temperature in the range 310°C-340°C.

The absolute pressure is comprised between atmospheric pressure (e.g. 0.101325 MPa) and 38 MPa, preferably between 5 MPa and 25 MPa and preferably between 6 MPa and 20 MPa.

Heating at this step (c) advantageously causes the second conditioned oil feedstock to liberate sulfur that can combine with the metal of the catalyst precursor composition.

According to one or more embodiments, the colloidal or molecular catalyst is formed, or at least starts forming, in situ within the second conditioned heavy oil feedstock at this step (c) of heating in the preheating device 230.

In order to form the colloidal or molecular catalyst, sulfur has to be available (e.g. as H_2S) to combine with the metal from the dispersed catalyst precursor composition.

Formation of the colloidal or molecular catalyst in situ within the second conditioned heavy oil feedstock

- 5 The general formation of the colloidal or molecular catalyst in situ within the second conditioned heavy oil feedstock is described in detail below, as well as the conditions required for such a formation at step (c) and/or step (d).

In the case where the heavy oil feedstock includes sufficient or excess sulfur, the final activated catalyst may be formed in situ by heating the second conditioned heavy oil feedstock to a
10 temperature sufficient to liberate the sulfur therefrom.

A source of sulfur can thus be H_2S dissolved in the heavy oil feedstock, or H_2S contained in hydrogen recycled to the hybrid bed hydroconversion reactor for hydroconversion or H_2S coming from organosulfur molecules present in the feedstock or possibly introduced beforehand in the heavy oil feedstock (injection of dimethyl disulfide, thioacetamide, any sulfur-containing hydrocarbon
15 feedstock of the type such as mercaptans, sulfides, sulfur-containing petroleum, sulfur-containing gas oil, sulfur-containing vacuum distillate, sulfur-containing residue), such an injection being rare and reserved for very atypical heavy oil feedstocks.

Thus a source of sulfur can be sulfur compounds within the feedstock or a sulfur compound added to the feedstock.

- 20 According to one or more embodiments, the formation of the dispersed colloidal or molecular catalyst is carried out with a total gauge pressure of between 0 MPa and 25 MPa.

Due to the thorough/intimate mixing at step (b), a molecularly-dispersed catalyst may form upon reacting with sulfur to form the metal sulfide compound. Under some circumstances, minor agglomeration may occur, yielding colloidal-sized catalyst particles. Simply adding together, while
25 failing to sufficiently mix, typically causes formation of large agglomerated metal sulfide compounds that are micron-sized or larger.

In order to form the metal sulfide catalyst, the second conditioned oil feedstock 105 is preferably heated to a temperature in a range of room temperature, e.g. $15^\circ C$, to $500^\circ C$, more preferably in a range of $200^\circ C$ to $500^\circ C$, even more preferably in a range of $250^\circ C$ to $450^\circ C$, and even more
30 preferably in a range of $300^\circ C$ to $435^\circ C$.

The temperature used at step (c) and/or (d) allows the formation of the metal sulfide catalyst.

The colloidal or molecular catalyst can thus be formed, at least in part, during this heating step (c), before the heated second conditioned oil feedstock is introduced into the hybrid bed hydroconversion reactor at step (d).

- 35 The colloidal or molecular catalyst can also be formed in situ within the hybrid bed hydroconversion reactor itself at step (d), especially either totally or in part in the case it has started to form at step (c).

The concentration of the metal of the catalyst, preferably molybdenum, in the conditioned oil feedstock is preferably in a range of 5 ppm to 500 ppm by weight of the heavy oil feedstock 101,
40 more preferably in a range of 10 ppm to 300 ppm by weight, more preferably in a range of 10 ppm to 175 ppm by weight, even more preferably in a range of 10 ppm to 75 ppm by weight, and most preferably in a range of 10 ppm to 50 ppm by weight.

The metal of the catalyst may become more concentrated as volatile fractions are removed from a non-volatile resid fraction.

Since the colloidal or molecular catalyst tends to be very hydrophilic, the individual particles or molecules will tend to migrate toward the more hydrophilic moieties or molecules within the heavy oil feedstock, especially asphaltenes. While the highly polar nature of the catalyst compound causes or allows the colloidal or the molecular catalyst to associate with asphaltene molecules, it is the general incompatibility between the highly polar catalyst compound and the hydrophobic heavy oil feedstock that necessitates the aforementioned intimate or thorough mixing of the oil soluble catalyst precursor composition within the heavy oil feedstock prior to formation of the colloidal or molecular catalyst.

Preferably, the colloidal or molecular catalyst comprises molybdenum disulfide.

Theoretically, a nanometer-sized crystal of molybdenum disulfide has 7 molybdenum atoms sandwiched in between 14 sulfur atoms, and the total number of molybdenum atoms exposed at the edge, thus available for catalytic activity, is greater than in a micron-sized crystal of molybdenum disulfide. In practical terms, forming small catalyst particles as in the present invention, i.e. colloidal or molecular catalyst, with an enhanced dispersion results in more catalyst particles and more evenly distributed catalyst sites throughout the oil feedstock. Moreover, nanometer-sized or smaller molybdenum disulfide particles are believed to become intimately associated with asphaltene molecules.

Step (d): Hydroconversion of the heated second conditioned heavy oil feedstock

The heated second conditioned feedstock 106 is then introduced, optionally pressurized by a pump, especially if not already pressurized before step (c), into at least one hybrid ebullated-entrained bed reactor 240 together with hydrogen 201, and is operated at hydroconversion conditions to produce an upgraded material 107.

As previously mentioned, the colloidal or molecular catalyst can form in situ within the hybrid bed hydroconversion reactor itself at step (d), if not totally formed or not formed at all at step (c).

When the colloidal or molecular catalyst is formed in situ within the second conditioned heavy oil feedstock at step (c), the heated second conditioned feedstock 106 already contains the colloidal or molecular catalyst, in part or in totality, when entering the at least one hybrid ebullated-entrained bed reactor 240.

The hybrid ebullated-entrained bed reactor 240 comprises a solid phase that includes a porous supported catalyst under the form an expanded bed, a liquid hydrocarbon phase comprising said heated second conditioned heavy oil feedstock 106 containing the colloidal or molecular catalyst dispersed therein, and a gaseous phase comprising hydrogen.

The hybrid ebullated-entrained bed reactor 240 is an ebullated bed hydroconversion reactor comprising the molecular or colloidal catalyst entrained out of the reactor with the effluents (upgraded feedstock), in addition to a porous supported catalyst, under the form of an expanded bed, maintained into the ebullated bed reactor.

According to one or more embodiments, the operation of the hybrid bed hydroconversion reactor is based on that of an ebullated bed reactor as used for the H-Oil™ process, such as described, for example, in patents US4521295 or US4495060 or US4457831 or US4354852 or in the paper Aiche, March 19-23, 1995, Houston, Texas, paper number 46d, "Second generation ebullated bed technology". In this implementation, the ebullated bed reactor can comprise a recirculation pump

which makes it possible to maintain the porous supported solid catalyst as an ebullated bed by continuous recycling of at least a part of a liquid fraction drawn off at the top of the reactor and reinjected at the bottom of the reactor.

The hybrid bed reactor preferably includes an input port located at or near the bottom of the hybrid bed reactor through which the heated second conditioned feedstock 106 is introduced together with hydrogen 201, and an output port at or near the top of the reactor through which the upgraded material 107 is withdrawn. The hybrid bed reactor further includes an expanded catalyst zone comprising the porous supported catalyst. The hybrid bed reactor also comprises a lower supported catalyst free zone located below the expanded catalyst zone, and an upper supported catalyst free zone above the expanded catalyst zone. The colloidal or molecular catalyst is dispersed throughout the feedstock within the hybrid bed reactor, including both the expanded catalyst zone and the supported catalyst free zones thereby being available to promote upgrading reactions within what constitute catalyst free zones in conventional ebullated bed reactors. Feedstock within the hybrid bed reactor is continuously recirculated from the upper supported catalyst free zone to the lower supported catalyst free zone by means of a recycling channel in communication with an ebullating pump. At the top of the recycling channel is a funnel-shaped recycle cup through which feedstock is drawn from the upper supported catalyst free zone. The internal recycled feedstock is blended with fresh heated second conditioned feedstock 106 and supplemental hydrogen gas 201.

As is known, and described for example in patent FR3033797, when it is spent, the porous supported hydroconversion catalyst may be partly replaced with fresh catalyst, by withdrawing the spent catalyst preferably at the bottom of the reactor, and by introducing fresh catalyst either at the top or at the bottom of the reactor. This replacement of spent catalyst is preferably performed at regular time intervals, and preferably portionwise or virtually continuously. These withdrawals / replacements are performed using devices which advantageously make possible the continuous functioning of this hydroconversion step. For example, input and output tubes opening into the expanded catalyst zone can be used for introducing/withdrawing respectively the fresh and spent supported catalyst.

The presence of colloidal or molecule catalyst within the hybrid bed reactor provides additional catalytic hydrogenation activity, both within the expanded catalyst zone, the recycle channel, and the lower and upper supported catalyst free zones. Capping of free radicals outside of the porous supported catalyst minimizes formation of sediment and coke precursors, which are often responsible for deactivating the supported catalyst. This can allow a reduction in the amount of porous supported catalyst that would otherwise be required to carry out a desired hydroprocessing reaction. It can also reduce the rate at which the porous supported catalyst must be withdrawn and replenished.

The hydroconversion porous supported catalyst used in hydroconversion step (d) may contain one or more elements from Groups 4 to 12 of the Periodic Table of the Elements, which are deposited on a support. The support of the porous support catalyst can advantageously be an amorphous support, such as silica, alumina, silica/alumina, titanium dioxide or combinations of these structures, and very preferably alumina.

The catalyst may contain at least one metal from Group VIII chosen from nickel and cobalt, preferably nickel, said element from Group VIII preferably being used in combination with at least one metal from Group VIB chosen from molybdenum and tungsten; preferably, the metal from Group VIB is molybdenum.

In the present description, the groups of chemical elements can be given according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, Editor in Chief D.R. Lide, 81st edition, 2000-2001). For example, Group VIII according to the CAS classification corresponds to the metals of columns 8, 9 and 10 according to the new IUPAC classification.

- 5 Advantageously, the hydroconversion porous supported catalyst used in the hydroconversion step (d) comprises an alumina support and at least one metal from Group VIII chosen from nickel and cobalt, preferably nickel, and at least one metal from Group VIB chosen from molybdenum and tungsten, preferably molybdenum. Preferably, the hydroconversion porous supported catalyst comprises nickel as element from Group VIII and molybdenum as element from Group VIB.
- 10 The content of metal from the non-noble group VIII, in particular of nickel, is advantageously between 0.5% and 10% by weight, expressed as weight of metal oxide (in particular NiO), and preferably between 1% and 6% by weight, and the content of metal from group VIB, in particular of molybdenum, is advantageously between 1% and 30% by weight, expressed as weight of metal oxide (in particular of molybdenum trioxide MoO₃), and preferably between 4% and 20% by weight. The
- 15 contents of metals are expressed as weight percentage of metal oxide relative to the weight of the porous supported catalyst.

This porous supported catalyst is advantageously used in the form of extrudates or of beads. The beads have, for example, a diameter of between 0.4 mm and 4.0 mm. The extrudates have, for example, a cylindrical form with a diameter of between 0.5 mm and 4.0 mm and a length of between

20 1 mm and 5 mm. The extrudates may also be objects of a different shape such as trilobes, regular or irregular tetralobes, or other multilobes. Porous supported catalysts of other forms may also be used.

The size of these various forms of porous supported catalysts may be characterized by means of the equivalent diameter. The equivalent diameter is defined as six times the ratio between the volume of

25 the particle and the external surface area of the particle. The porous supported catalyst used in the form of extrudates, beads or other forms thus has an equivalent diameter of between 0.4 mm and 4.4 mm. These porous supported catalysts are well known to those skilled in the art.

In the hydroconversion step (d), said heated second conditioned feedstock 106 is generally converted under conventional conditions for hydroconversion of a heavy oil feedstock.

- 30 According to one or more embodiments, the hydroconversion step (d) is carried out under an absolute pressure of between 2 and 38 MPa, preferably between 5 and 25 MPa and preferably between 6 and 20 MPa, and at a temperature between 300°C and 550°C, preferably between 350°C and 500°C, preferably between 370°C and 450°C, more preferably between 400°C and 440°C, and even more preferably between 410°C and 435°C.
- 35 According to one or more embodiments, the liquid hourly space velocity (LHSV) of the feedstock relative to the volume of each hybrid reactor is between 0.05 h⁻¹ and 10 h⁻¹, preferably between 0.10 h⁻¹ and 2 h⁻¹ and preferably between 0.10 h⁻¹ and 1 h⁻¹. According to another embodiment, the LHSV is between 0.05 h⁻¹ and 0.09 h⁻¹. LHSV is defined as the liquid feed volumetric flow rate at room temperature and atmospheric pressure (typically 15°C and 0.101325 MPa) per reactor volume.
- 40 According to one or more embodiments, the amount of hydrogen mixed with the heavy oil feedstock 106 is preferably between 50 and 5000 normal cubic meters (Nm³) per cubic meter (m³) of liquid heavy oil feedstock, such as between 100 and 3000 Nm³/m³ and preferably between 200 and 2000 Nm³/m³.

According to one or more embodiments, the hydroconversion step (d) is carried out in one or more hybrid bed hydroconversion reactors, which can be in series and/or in parallel.

Step (e): Further processing of the upgraded material from hydroconversion step (d)

The upgraded material 107 can be further processed.

- 5 Examples of such further processing comprise, without limitation, at least one from among: a separation of hydrocarbon fractions of the upgraded material, a further hydroconversion in one or more supplemental hybrid ebullated-entrained bed reactors or ebullated bed reactors to produce a further upgraded material, a fractionation of hydrocarbon cuts of the further upgraded material, a deasphalting of at least a part of the upgraded material 107 or a heavy liquid fraction resulting from
10 a fractionation of the upgraded material or a further upgraded material, a purification in a guard bed of the upgraded or further upgraded material to remove at least a portion of the colloidal or molecular catalyst and metal impurities.

- The various hydrocarbon fractions that can be produced from the upgraded material 107 can be sent to different processes in the refinery, and details on these post-processing operations are not
15 described herein as they are generally known to the skilled person and will complicate the description to no purpose. For example, gas fractions, naphtha, middle distillates, VGO, DAO can be sent to processes of hydrotreating, steam cracking, fluid catalytic cracking (FCC), hydrocracking, lubricating oil extraction, etc., residues (atmospheric or vacuum residues) can also be post-processed, or used for other applications like gasification, bitumen production etc. Heavy fractions,
20 including residues, can also be recycled in the hydroconversion process, for example in the hybrid bed reactor.

- According to one or more embodiments, as illustrated in figure 2, the process further comprises:
- a second hydroconversion step in a second hybrid ebullated-entrained bed reactor 260 in the presence of hydrogen 204 of at least a portion or all of the upgraded material resulting from the
25 hydroconversion step (d) or optionally of a liquid heavy fraction 203 that boils predominantly at a temperature greater than or equal to 350°C resulting from an optional separation step separating a portion or all of the upgraded material resulting from the hydroconversion step (d), said second hybrid ebullated-entrained bed reactor 260 comprising a second porous supported catalyst and operating at hydroconversion conditions to produce a hydroconverted liquid effluent 205 with a
30 reduced heavy residue fraction, a reduced Conradson carbon residue, and possibly a reduced quantity of sulfur, and/or nitrogen, and/or metals;
 - a step of fractionating a portion or all of said hydroconverted liquid effluent 205 in a fractionation section 270 to produce at least one heavy cut 207 that boils predominantly at a temperature greater than or equal to 350°C, said heavy cut containing a residual fraction that boils at a temperature
35 greater than or equal to 540°C;
 - an optional step of deasphalting a portion or all of said heavy cut 207 in a deasphalter 280 with at least one hydrocarbon solvent to produce a deasphalted oil DAO 208 and a residual asphalt 209.
- Said second hydroconversion step is performed in a manner similar to that which was described for the hydroconversion step (d), and its description is not therefore repeated here. This applies notably
40 for the operating conditions, the equipment used, the hydroconversion porous supported catalysts used, with the exception of the specifications given below.

As for the hydroconversion step (d), the second hydroconversion step is performed in a second hybrid ebullated-entrained bed reactor 260 similar to hybrid bed reactor 240.

In this additional hydroconversion step, the operating conditions may be similar or different from those in the hydroconversion step (d), the temperature remaining within the range between 300°C and 550°C, preferably between 350°C and 500°C, and more preferably between 370°C and 450°C, more preferably between 400°C and 440°C, and even more preferably between 410°C and 435°C, and the amount of hydrogen introduced into the reactor remains within the range between 50 and 5000 Nm³/m³ of liquid feedstock, preferably between 100 and 3000 Nm³/m³, and even more preferably between 200 and 2000 Nm³/m³. The other pressure and LHSV parameters are within ranges identical to those described for the hydroconversion step (d).

The hydroconversion porous supported catalyst used in the second hybrid bed reactor 260 may be the same as that used in hybrid bed reactor 240, or may also be another porous supported catalyst also suitable for hydroconversion of heavy oil feedstocks, as defined for the supported catalyst used in hydroconversion step (d).

The optional separation step, separating a portion or all of the upgraded material 107 to produce at least two fractions including the heavy liquid fraction 203 that boils predominantly at a temperature greater than or equal to 350°C, is carried out in a separation section 250.

The other cut(s) 202 are light and intermediate cut(s). The light fraction thus separated contains mainly gases (H₂, H₂S, NH₃, and C₁-C₄), naphtha (fraction that boils at a temperature below 150°C), kerosene (fraction that boils between 150°C and 250°C), and at least one portion of the diesel (fraction that boils between 250°C and 375°C). The light fraction may then be sent at least partly to a fractionating unit (not represented in figure 2) where the light gases are extracted from said light fraction, for example by passing through a flash drum. The gaseous hydrogen thus recovered, which can have been sent to a purification and compression equipment, may advantageously be recycled into the hydroconversion step (d). The recovered gaseous hydrogen can also be used in other equipment of the refinery.

The separation section 250 comprises any separation means known to a person skilled in the art. It can comprise one or more flash drums arranged in series, and/or one or more steam- and/or hydrogen-stripping columns, and/or an atmospheric distillation column, and/or a vacuum distillation column, and is preferably constituted by a single flash drum, commonly known as a "hot separator".

The step of fractionating, separating a portion or all of the hydroconverted liquid effluent from the second hydroconversion step to produce at least two fractions including the at least one heavy liquid cut 207 that boils predominantly at a temperature above 350°C, preferably above 500°C and preferably above 540°C, is carried out in the fractionation section 270 comprising any separation means known to a person skilled in the art. The other cut(s) 206 are light and intermediate cut(s). The heavy liquid cut 207 contains a fraction that boils at a temperature above 540°C, referred to as vacuum residue (which is the unconverted fraction). It may contain a portion of the diesel fraction that boils between 250°C and 375°C and a fraction that boils between 375°C and 540°C referred to as vacuum distillate.

The fractionation section 270 can comprise one or more flash drums arranged in series, and/or one or more steam and/or hydrogen-stripping columns, and/or an atmospheric distillation column, and/or a vacuum distillation column, and is preferably constituted by a set of several flash drums in series and atmospheric and vacuum distillation columns.

Where it is desired to recycle a part of the heavy resid fraction (e.g. part of the heavy liquid cut 207 and/or part of the residual asphalt 209, or part of DAO 208) back through the hydroconversion system (e.g. for example in hybrid bed reactor 240 or upstream) it may be advantageous to leave the

colloidal or molecular catalyst within the resid, and/or residual asphalt fraction. A purging on the recycled stream can be carried out, in general for preventing some compounds from accumulating at excessive levels.

The present invention also relates to an ebullated-entrained bed system 200 configured for

- 5 hydroconverting the heavy oil feedstock 101 as detailed above. Numerical references mentioned below relate to figure 2, which illustrates schematically an example of a hybrid bed hydroconversion system according to the invention. Said system 200 comprises:
- the first conditioner mixer 210 configured to prepare a first conditioned heavy oil feedstock 103 by mixing said heavy oil feedstock 101 with an organic chemical compound 102 comprising at least one
 - 10 carboxylic acid function and/or at least one ester function and/or an acid anhydride function ;
 - a second conditioner mixer 220 configured to prepare a second conditioned heavy oil feedstock 105 by mixing a catalyst precursor composition 104 with said first conditioned heavy oil feedstock 103 ;
 - at least one preheating device 230 configured to heat the second conditioned feedstock 105 ;
 - the at least one hybrid ebullated-entrained bed reactor 240 configured to comprise :
 - 15 -- an expanded catalyst bed comprising a solid phase that includes a porous supported catalyst as a solid phase,
 - a liquid hydrocarbon phase comprising said second heated conditioned heavy oil feedstock 106 containing the colloidal or molecular catalyst dispersed therein;
 - and a gaseous phase comprising hydrogen.
 - 20 Said at least one hybrid ebullated-entrained bed reactor 240 is configured to operate in the presence of hydrogen and at hydroconversion conditions in order to cause thermal cracking of hydrocarbons in said second conditioned heavy oil feedstock to provide an upgraded material 107.

Said at least one preheating device 230 and/or said at least one hybrid ebullated-entrained bed reactor 240 are also configured to form the colloidal or molecular catalyst within said second

25 conditioned heavy oil feedstock.

Details on each apparatus/device/section used in the ebullated-entrained bed system have already been given above in relation to the process and are not repeated.

Example

The following example illustrates, without limiting the scope of the invention, some of the

30 performance qualities of the process and system according to the invention, in particular the reduced fouling of equipment, in comparison with a process and system according to the prior art.

The example is based on a test using an analytical device, called Alcor Hot Liquid Process Simulator, or HLPS, simulating the fouling effect of atmospheric residues (AR) in heat exchangers. The AR is pumped through a heater tube (laminar flow tube-in-shell heat exchanger) under controlled

35 conditions and fouling deposits are formed on the heater tube. The temperature of the AR which exits the heat exchanger is related to the effect of the deposits on the efficiency of the heat exchanger. The decrease in AR liquid outlet temperature from its initial maximum value is called Delta T and is correlated to the deposit quantity. The higher the decreasing of Delta T, the higher the fouling and the deposit quantity.

40 The HLPS test can be used to evaluate the fouling tendency of different ARs by comparing the decreasing slope of the AR liquid outlet temperature obtained under identical test conditions. The effectiveness of an organic additive can also be determined by comparing test results from a neat sample (without an organic additive) to the sample blended with the organic additive.

Three samples are tested: sample 1 is a blend of a heavy oil feedstock and a molecular or colloidal catalyst according to the prior art, and samples 2 and 3 are blends according to the invention of a heavy oil feedstock with an organic additive, in addition to the same molecular or colloidal catalyst.

The heavy oil feedstock ("Feed") is an atmospheric residue (AR) whose main composition and properties are given table 1 below.

[Table 1]

	Standardized method	Unit	Feed	VGO (CPC diluent)
Density	NF EN ISO 12185		0.959	0.8677
IBP-350°C	ASTM D1160	wt %	21	2.7
350-540°C	ASTM D1160	wt %	35	95.5
540°C+	ASTM D1160	wt %	44	1.8
C	ASTM D5291	wt %	84.5	86.5
H	ASTM D5291	wt %	11.4	13.71
N	ASTM D5291	wt %	0.3	0.0037
S	NF ISO 8754	wt %	3.81	0.074
Ni	ASTM D7260	wt ppm	25	<2
V	ASTM D7260	wt ppm	78	<2
K	ASTM D7260	wt ppm	2	<1
Na	ASTM D7260	wt ppm	196	<1
Ca	ASTM D7260	wt ppm	<1	<1
P	ASTM D7260	wt ppm	<5	<5
Si	ASTM D7260	wt ppm	<1	<1
Fe	ASTM D7260	wt ppm	3	6
Ti	ASTM D7260	wt ppm	79	<1
Asphaltenes C ₅	UOP99 - 07	wt %	10.6	0.2
Asphaltenes C ₇	NF T60-115	wt %	4.7	0.05
Conradson Carbon	NF EN ISO 10370	wt %	11.3	0.2

Sample 1: sample 1 is a blend of the Feed (AR) and a catalyst precursor composition (CPC) being molybdenum 2-ethylhexanoate, the molybdenum 2-ethylhexanoate being diluted in a vacuum gas oil (VGO) to form a CPC solution.

10 The composition of the VGO is given in table 1 above.

The CPC solution is obtained by mixing the molybdenum 2-ethylhexanoate with the VGO, at a temperature of 70°C and for a time period of 30 minutes. The molybdenum content in the solution of CPC containing VGO is 3500 wt. ppm.

15 The solution of CPC is then mixed with the Feed (AR) at a temperature of 70°C and for a time period of 30 minutes.

The content of Mo in sample 1 is of 315 wt. ppm (see table 2 below).

Sample 2: sample 2 is a blend of Feed (AR) with the same CPC solution (molybdenum 2-ethylhexanoate diluted with the VGO) as in sample 1, and with an organic additive being 2-Ethylhexanoic Acid (2EHA). The CAS number of 2EHA is 149-57-5.

20 The Feed is first mixed with the organic additive 2EHA, for a time period of 30 min, and at temperature of 70°C, to form a first conditioned feedstock.

Then, the first conditioned feedstock is mixed with the solution of CPC, obtained as detailed for sample 1, at a temperature of 70°C and for a time period of 30 minutes, to form a second conditioned feedstock which is sample 2.

The content of Mo in sample 2 is of 315 wt. ppm (see table 2 below).

- 5 The concentration of the organic additive 2EHA is 5827 wt. ppm (see table 2 below).

The molar ratio of 2EHA/Mo = 12.3

Sample 3: sample 3 is a blend of Feed (AR) with the same CPC solution (molybdenum 2-ethylhexanoate diluted with the VGO) as in samples 1 and 2, and with an organic additive which is Ethyl octanoate (EO). The CAS number of the EO is 106-32-1.

- 10 The Feed is first mixed with the organic additive EO, for a time period of 30 min, and at temperature of 70°C, to form a first conditioned feedstock.

Then, the first conditioned feedstock is mixed with the CPC solution, obtained as detailed for sample 1, at a temperature of 70°C and for a time period of 30 minutes, to form a second conditioned feedstock which is sample 3.

- 15 The content of Mo in sample 3 is of 315 wt. ppm (see table 2 below).

The concentration of the organic additive EO in sample 3 is equal to 7340 ppm by weight (see table 2 below).

The molar ratio of EO/Mo = 13.0

[Table 2]

	Sample 1 : Feed + CPC in VGO	Sample 2 : [Feed + 2EHA] CPC in VGO	Sample 3 : [Feed + EO] + CPC in VGO
Mo (wt ppm)	315	315	315
Acid organic additive 2EHA (wt ppm)	-	5827	-
Ester organic additive EO (wt ppm)	-	-	7340

- 20 The Mo content in the samples was determined according to ASTM D7260. The acid and ester organic additive content was determined by weighing.

The HLPS test conditions are given in table 3 below.

[Table 3]

Test mode	Single pass
Feed temperature (°C)	90
Flow rate (mL/min)	1
Oil in temperature (°C)	100
Tube temperature (°C)	450
Tube material	1018 steel
Gauge Pressure (MPa)	3.4

- 25 The results of the test for the different samples (S_1 for sample 1, S_2 for sample 2, S_3 for sample 3) are shown in the graph of figure 3. X-axis represents time in hours, and Y-axis represents the difference in temperature ΔT between the temperature of the oil blend (sample) exiting the tube at a time t [$T_{Oil Out}$] $_t$ and the maximum temperature of the oil blend (sample) exiting the tube [$T_{Oil Out}$] $_{Max}$. $\Delta T = [T_{Oil Out}]_t - [T_{Oil Out}]_{Max}$.

The results show that the sample 1 has a strong fouling tendency since its Delta T falls quickly. Samples 2 and 3 which contain an organic additive, e.g. 2EHA or EO, according to the invention have a lower Delta T than sample 1, showing that the fouling behavior is significantly reduced under the action of said organic additive.

Claims

1. A process for the hydroconversion of a heavy oil feedstock (101) containing a fraction of at least 50% by weight having a boiling point of at least 300°C, and containing metals and asphaltenes, comprising the following steps :
 - 5 (a) preparing a first conditioned heavy oil feedstock (103) by blending said heavy oil feedstock (101) with an organic chemical compound (102) comprising at least one carboxylic acid function and/or at least one ester function and/or an acid anhydride function;
 - (b) preparing a second conditioned heavy oil feedstock (105) by mixing a catalyst precursor composition (104) with the first conditioned heavy oil feedstock (103) from step (a) in a manner such
 - 10 that a colloidal or molecular catalyst is formed when it reacts with sulfur;
 - (c) heating the second conditioned heavy oil feedstock from step (b) in at least one preheating device;
 - d) introducing said heated second conditioned heavy oil feedstock (106) from step (c) into at least one hybrid ebullated-entrained bed reactor comprising a hydroconversion porous supported catalyst
 - 15 and operating said hybrid ebullated-entrained bed reactor in the presence of hydrogen and at hydroconversion conditions to produce an upgraded material (107), and wherein the colloidal or molecular catalyst is formed *in situ* within the second conditioned heavy oil feedstock at step (c) and/or at step (d).
2. The process as claimed in claim 1, wherein step (a) comprises mixing said organic chemical compound (102) and said heavy oil feedstock (101) in a dedicated vessel of an active mixing device.
- 20 3. The process as claimed in claim 1, wherein step (a) comprises injecting said organic chemical compound (102) into a pipe conveying said heavy oil feedstock (101) toward the hybrid ebullated-entrained bed reactor.
4. The process as claimed in any one of the preceding claims, wherein step (a) is carried out at a
- 25 temperature comprised between room temperature and 300°C, preferably between 70°C and 200°C, and the residence time of the organic chemical compound with said heavy oil feedstock before step (b) is between 1 second and 10 hours.
5. The process as claimed in any one of the preceding claims, wherein the organic chemical compound (102) is selected from the group consisting of 2-ethylhexanoic acid, naphthenic acid,
- 30 caprylic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, ethyl octanoate, ethyl 2-ethylhexanoate, 2-ethylhexyl 2-ethylhexanoate, benzyl 2-ethylhexanoate, diethyl adipate, dimethyl adipate, bis(2-ethylhexyl) adipate, dimethyl pimelate, dimethyl suberate, monomethyl suberate, hexanoic anhydride, caprylic anhydride, and a mixture thereof.
6. The process as claimed in claim 5, wherein the organic chemical compound (102) comprises 2-ethylhexanoic acid, and preferably is 2-ethylhexanoic acid.
- 35 7. The process as claimed in claim 5, wherein the organic chemical compound (102) comprises ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate, and is preferably ethyl octanoate or 2-ethylhexyl 2-ethylhexanoate.
8. The process as claimed in any one of the preceding claims, wherein the catalyst precursor
- 40 composition (104) comprises an oil soluble organo-metallic or bimetallic compound or complex, preferably an oil soluble organo-metallic compound or complex selected from the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate, vanadium naphthanate, vanadium

octoate, molybdenum hexacarbonyl, vanadium hexacarbonyl, and iron pentacarbonyl, and is preferably molybdenum 2-ethylhexanoate.

9. The process as claimed in any one of the preceding claims, wherein the molar ratio between said organic chemical compound (102) added at step a) and the active metal(s), preferably molybdenum, of the catalyst precursor composition (104) added at step (b), in said second conditioned heavy oil feedstock is comprised between 0.1:1 and 20:1.

10. The process as claimed in any one of the preceding claims, wherein the colloidal or molecular catalyst comprises molybdenum disulfide.

11. The process as claimed in any one of the preceding claims, wherein step (b) comprises: (b1) pre-mixing the catalyst precursor composition with a hydrocarbon oil diluent below a temperature at which a substantial portion of the catalyst precursor composition begins to decompose thermally in order to form a diluted precursor mixture; and (b2) mixing said diluted precursor mixture with the first conditioned heavy oil feedstock.

12. The process as claimed in claim 11, wherein step (b1) is carried out at a temperature between room temperature and 300°C and for a period of time from 1 second to 30 minutes, and step (b2) is carried out at a temperature between room temperature and 300°C and for a period of time from 1 second to 30 minutes.

13. The process as claimed in any one of the preceding claims, wherein step (c) comprises heating at a temperature between 280°C and 450°C, more preferably between 300°C and 400°C, and even more between 320°C and 365°C.

14. The process as claimed in any one of the preceding claims, wherein the heavy oil feedstock (101) comprises at least one of the following feedstocks: heavy crude oil, oil sand bitumen, atmospheric tower bottoms, vacuum tower bottoms, resid, visbreaker bottoms, coal tar, heavy oil from oil shale, liquefied coal, heavy bio oils, and heavy oils comprising plastic waste and/or a plastic pyrolysis oil.

15. The process as claimed in any one of the preceding claims, wherein the heavy oil feedstock (101) has a sulfur at a content of greater than 0.5% by weight, a Conradson carbon residue of at least 0.5% by weight, C₇ asphaltenes at a content of greater than 1% by weight, transition and/or post-transition and/or metalloid metals at a content of greater than 2 ppm by weight, and alkali and/or alkaline earth metals at a content of greater than 2 ppm by weight.

16. The process as claimed in any one of the preceding claims, wherein said hydroconversion step (d) is carried out under an absolute pressure of between 2 MPa and 38 MPa, at a temperature of between 300°C and 550°C, at a liquid hourly space velocity LHSV relative to the volume of each hybrid reactor of between 0.05 h⁻¹ and 10 h⁻¹ and under an amount of hydrogen mixed with the feedstock entering the hybrid bed reactor of between 50 and 5000 normal cubic meters (Nm³) per cubic meter (m³) of feedstock.

17. The process as claimed in any one of the preceding claims, wherein the concentration of the catalyst metal, preferably molybdenum, in the second conditioned oil feedstock (105) is in a range of 5 ppm to 500 ppm by weight of the heavy oil feedstock.

18. The process as claimed in any one of the preceding claims, further comprising a step (e) of further processing the upgraded material, said step (e) comprising:

- a second hydroconversion step in a second hybrid ebullated-entrained bed reactor (260) of at least a portion or all of the upgraded material resulting from the hydroconversion step (d) or optionally of

a liquid heavy fraction that boils predominantly at a temperature greater than or equal to 350°C resulting from an optional separation step separating a portion or all of the upgraded material resulting from the hydroconversion step (d), said second hybrid ebullated-entrained bed reactor (260) comprising a second porous supported catalyst and operating in the presence of hydrogen (204) and at hydroconversion conditions to produce a hydroconverted liquid effluent (205) with a reduced Conradson carbon residue, and possibly a reduced quantity of sulfur, and/or nitrogen, and/or metals,

- a step of fractionating a portion or all of said hydroconverted liquid effluent (205) in a fractionation section (270) to produce at least one heavy cut (207) that boils predominantly at a temperature greater than or equal to 350°C, said heavy cut containing a residual fraction that boils at a temperature greater than or equal to 540°C;

- an optional step of deasphalting, in a deasphalter (280), a portion or all of said heavy cut (207) with at least one hydrocarbon solvent to produce a deasphalted oil DAO and a residual asphalt; and wherein, said hydroconversion step (d) and said second hydroconversion step are carried out under an absolute pressure of between 2 and 38 MPa, at a temperature of between 300°C and 550°C, at a liquid hourly space velocity LHSV relative to the volume of each hybrid ebullated-entrained bed reactor of between 0.05 h⁻¹ and 10 h⁻¹ and under an amount of hydrogen mixed with the feedstock entering each hybrid ebullated-entrained bed reactor of between 50 and 5000 normal cubic meters (Nm³) per cubic meter (m³) of feedstock.