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(54) **EBULLATED OR HYBRID EBULLATED-BED
HYDROCONVERSION OF A FEEDSTOCK
COMPRISING A FRACTION OF PLASTIC
PYROLYSIS OIL AND/OR SOLID
RECOVERY FUELS**

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(71) Applicant: **IFP Energies Nouvelles**,
Rueil-Malmaison (FR)

(72) Inventors: **Matthieu DREILLARD**,
Rueil-Malmaison Cedex (FR); **Joao**
MARQUES, Rueil-Malmaison Cedex
(FR); **Wilfried WEISS**,
Rueil-Malmaison Cedex (FR); **Duc**
NGUYEN-HONG, Rueil-Malmaison
(FR)

(73) Assignee: **IFP Energies Nouvelles**,
Rueil-Malmaison (FR)

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ABSTRACT

The present invention relative to a process for the hydro-conversion of a feedstock including a fraction of less than 50% by weight of plastic and/or SRF pyrolysis oil (**102**) and a heavy hydrocarbon fraction (**101**) containing a portion of at least 50% by weight with a boiling point of at least 300° C. and containing sulfur and nitrogen. The hydroconversion uses one or more ebullated bed or hybrid ebullated-entrained bed reactors (**20**), and preferably two successive hydroconversion steps. The process according to the invention allows the production of higher-quality, lower-boiling materials, for example for the production of fuels or chemical compounds for the petrochemical industry, with improved yields of certain cuts and while allowing facilitated processing of the hydroconverted products in downstream steps such as fixed-bed hydrotreatment and while maintaining good stability of the unconverted fraction.

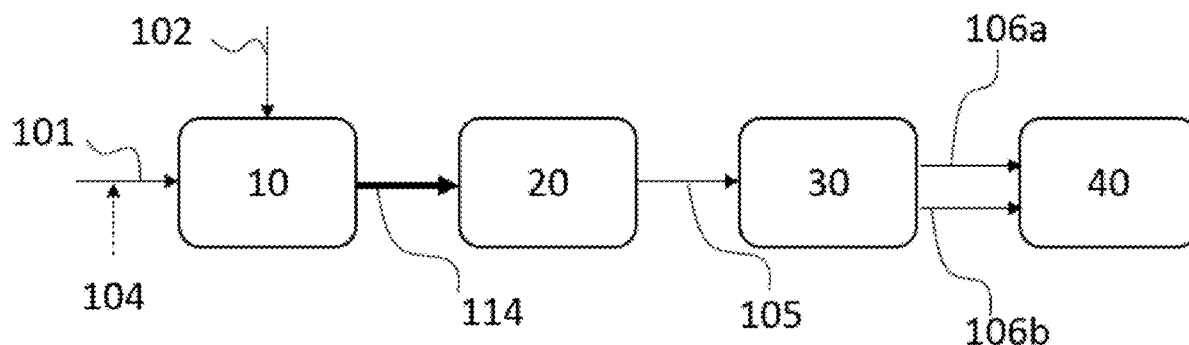


Fig. 1

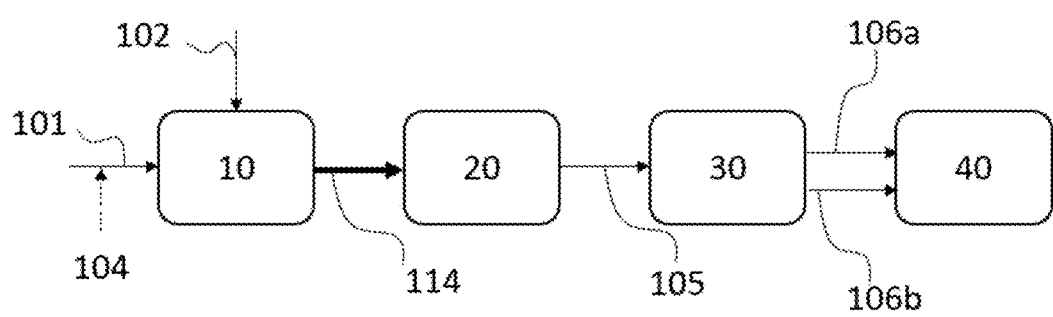
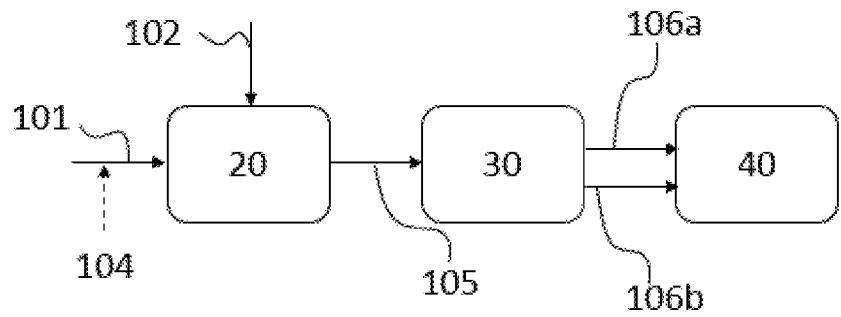


Fig. 2



**EBULLATED OR HYBRID EBULLATED-BED
HYDROCONVERSION OF A FEEDSTOCK
COMPRISING A FRACTION OF PLASTIC
PYROLYSIS OIL AND/OR SOLID
RECOVERY FUELS**

TECHNICAL FIELD

[0001] The present invention relates to the field of hydro-conversion of feedstocks predominantly including heavy hydrocarbon fraction, notably a heavy hydrocarbon fraction containing a portion of at least 50% by weight, preferably at least 80% by weight, having a boiling point of at least 300° C., and a minor fraction of plastic pyrolysis oil and/or solid recovered fuel (SRF) pyrolysis oil, laden with impurities. The heavy hydrocarbon fraction may be a crude oil or may result from the distillation and/or refining of a crude oil, typically a topped crude oil, a residue from the atmospheric and/or vacuum distillation of a crude oil. Preferably, the heavy hydrocarbon fraction is of the vacuum residue type composed of at least 50% by weight, preferably of at least 80% by weight, of hydrocarbons having a boiling point of at least 450° C.

[0002] In particular, the present invention relates to a process for the hydroconversion of such a mixed feedstock, including at least one hydroconversion step using one or more reactors operating in an ebullated bed or a hybrid ebullated-entrained bed, and preferably two successive hydroconversion steps, with a view to producing higher-quality, lower-boiling point materials, for example for fuel production or chemical product production purposes, while at the same time enabling the scavenging of impurities from the plastic pyrolysis oil and/or SRF pyrolysis oil.

PRIOR ART

[0003] Over the past few years, the fuel and chemical industries have seen the emergence of processes incorporating products other than conventional petroleum products, for example products of renewable origin such as plant and animal oils or oils from waste materials, for instance plastics or spent oils, in addition to or as a replacement for products of fossil origin.

[0004] In particular, plastics resulting from collection and sorting industries can undergo a step of pyrolysis in order to obtain, inter alia, pyrolysis oils. These plastic pyrolysis oils are generally incinerated in order to generate electricity and/or used as fuel in industrial or urban heating boilers.

[0005] Solid recovered fuels (SRFs), also called refuse-derived fuel (RDF), are solid non-hazardous wastes prepared with a view to energy recovery, whether they originate from household and similar waste, from waste from economic activities or from waste from construction and demolition. SRFs are generally a mixture of any combustible waste, such as used tyres, food by-products (fats, animal meal, and the like), viscose and wood waste, light fractions resulting from shredders (for example from used vehicles, electrical and electronic equipment (WEEE), household and commercial waste, residues from the recycling of various types of waste, including certain municipal wastes, plastic waste, textiles or wood, inter alia. SRFs generally contain plastic waste. Nowadays, SRFs are mainly upgraded as energy. They can be used directly as substitutes for fossil fuels in co-incineration facilities (coal and lignite power stations, cement works, lime kilns) or in household waste

incineration units, or indirectly in pyrolysis units dedicated to energy upgrading: SRF pyrolysis oils are thus generally burned to generate electricity, or even are used as fuel in industrial or urban heating boilers.

[0006] Plastic pyrolysis oils and SRF pyrolysis oils can also be upgraded via refining processes, to produce fuels, for example petrol or diesel, and/or chemicals, such as olefins, for the production of various polymers of the chemical industry.

[0007] However, this other route for the upgrading of plastic pyrolysis oils and SRF pyrolysis oils is confronted with the problems generated by the specific composition of these oils, in particular by the impurities which they contain, the composition of these oils being itself related to the diversity of the components of the plastic waste or SRFs.

[0008] Specifically, plastic waste or SRFs are generally mixtures of several polymers, for example mixtures of polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride and polystyrene. In addition, depending on the uses, plastics may contain other compounds in addition to the polymers, such as plasticizers, pigments, dyes or polymerization catalyst residues, and also other highly varied organic and mineral impurities, originating from separation operations in sorting centers, the selectivity of which operation may not be total.

[0009] The oils resulting from plastic pyrolysis or from SRF pyrolysis thus generally comprise many diolefins and impurities, in particular metals, silicon, or also halogenated compounds, notably chlorine-based compounds, heteroelements, such as sulfur, oxygen and nitrogen, insolubles, at contents which are often high and which may be incompatible with certain refining units, for instance fixed-bed hydrotreating units.

[0010] The treatment of these oils can present operability problems and notably problems of corrosion, coking or catalytic deactivation, or also incompatibility problems in the applications of the target polymers. The presence of diolefins, for example, very often results in problems of instability of the pyrolysis oil which are characterized by the formation of gums. The gums and the insolubles possibly present in the pyrolysis oil can give rise to problems of clogging in the items of equipment.

[0011] Patent application WO 2018/055555 provides, for example, a very general and relatively complex overall process for the recycling of plastic waste, ranging from the actual step of pyrolysis of the plastic waste up to a steam cracking step, which makes it possible to produce products that are highly upgradable in the petrochemical field, such as olefins and aromatic compounds. The process comprises, inter alia, a step of hydrocracking of the liquid phase resulting directly from the pyrolysis, preferably in a fixed bed.

[0012] Patent applications FR 3 107 530, FR 3 113 060 and FR 3 113 061 describe processes for the treatment of a plastic pyrolysis oil including, inter alia, a step of selective hydrogenation of the plastic pyrolysis oil and fixed-bed hydrotreating of the hydrogenated effluent. The naphtha cut resulting from a specific separation with water of the hydrotreated effluent, followed by fractionation of the separated hydrocarbon stream, can be sent to a steam cracker or be used as fuel base. According to patent applications FR 3 113 060 and FR 3 113 061, the process incorporates one or two steps of hydrocracking in a fixed bed after the hydrotreating step in order to minimize the yield of the

heavy cut and to maximize the yield of the naphtha cut by transforming the heavy cut, at least partly, into a naphtha cut by hydrocracking, which is the cut generally favored for a steam cracking unit.

[0013] Due to the content of impurities in plastic pyrolysis oils, notably when they are heavily laden with impurities, deactivation of the catalysts of the hydrotreatment unit which is operated in a fixed bed may be observed, which reduces the cycle time. Indeed, the main constraint of fixed-bed units is the fact that the unit has to be shut down to replace the catalysts. In addition, plastic pyrolysis oils, notably those heavily laden with diolefins and impurities, can create clogging problems notably in preheating furnaces, feedstock/effluent exchangers or on the bed heads of fixed-bed catalytic reactors.

[0014] Unpublished patent application FR 20/09750 describes a process for treating plastic pyrolysis oil and/or SRF pyrolysis oil comprising, inter alia, ebullated-bed, entrained-bed and/or moving-bed hydroconversion of the optionally pre-hydrogenated feedstock. The feedstock contains at least 50% by weight of plastic pyrolysis oil and/or SRF pyrolysis oil, and is preferably constituted of plastic pyrolysis oil and/or SRF pyrolysis oil. After successive steps of separation with water, fractionation of the separated hydrocarbon-based stream, hydrotreatment of the 385° C.—cut and fractionation of the hydrotreated stream, a liquid effluent suitable for a steam cracking unit is obtained. The use of an ebullated, entrained and/or moving bed hydroconversion step allows long hydroconversion unit cycle times, as a result of the conventional use in this type of unit of a system for adding fresh catalyst and withdrawing spent catalyst without stopping the unit. This compensates for catalyst deactivation, which may be caused by feedstock impurities, unlike in fixed-bed reactors in which clogging of the catalyst beds is a problem. Furthermore, this hydroconversion step upstream of hydrotreatment allows longer hydrotreatment unit cycle times by virtue of the hydrotreatment reactions performed partly upstream in the hydroconversion unit, and simpler hydrotreatment due to the conversion of at least part of the heavy compounds into lighter compounds during hydroconversion.

[0015] Unpublished patent application FR 21/04873 describes a process for treating plastic pyrolysis oil and/or SRF pyrolysis oil which is similar to that of patent application FR 20/09750, in which there is notably no separation step between the hydroconversion step and the hydrotreatment step.

[0016] Unpublished patent application FR 21/04874 describes a process for the simultaneous treatment of a plastic pyrolysis oil and a feedstock from renewable sources, such as a plant oil, which is similar to that of patent application 21/04873, in which the plastic pyrolysis oil, optionally hydrogenated beforehand, is sent to a hydrodemetallization step, and the demetallized effluent is then sent to a hydrotreatment step. The hydrodemetallization and hydrotreatment steps may be performed in an ebullated bed. Feedstock from renewable sources is fed to the hydrogenation step, and/or to the hydrodemetallization step and/or to the hydrotreatment step.

Objectives and Summary of the Invention

[0017] The present invention falls within the field of upgrading heavy feedstocks which are difficult to upgrade, such as petroleum residues, which generally contain high

levels of impurities such as metals, sulfur, nitrogen, Conradson carbon and asphaltenes, in order to convert them into lighter products that can be upgraded as fuels, for example to produce gasolines or gas oils, or raw materials for the petrochemical industry.

[0018] The inventors have demonstrated that, in a surprising manner, it is possible to incorporate a minor fraction of plastic pyrolysis oil and/or SRF pyrolysis oil, laden with impurities, into a fossil-based heavy hydrocarbon feedstock, typically a vacuum residue, traditionally treated in an ebullated bed or hybrid ebullated-entrained bed hydroconversion process, and thus to improve the production of fuel base and/or other upgradable hydrocarbons, while at the same time scavenging in the supported catalyst of the hydroconversion step the impurities initially present in the pyrolysis oil, such as silicon, thus allowing easier processing of the products in downstream steps such as fixed-bed hydrotreatment, and while maintaining good stability of the unconverted fraction.

[0019] The present invention thus proposes a process for the hydroconversion of a fossil-based heavy hydrocarbon feedstock, notably of the vacuum residue type, in an ebullated bed or a hybrid ebullated-entrained bed, said feedstock including a minor fraction of plastic pyrolysis oil and/or SRF pyrolysis oil, thus allowing the production of fuel base and other upgradable hydrocarbons, and thus the upgrading of said fraction.

[0020] Thus, to overcome the problems of the prior art set out above, and to achieve at least one of the abovementioned objectives, among others, the present invention proposes, according to a first aspect, a process for hydroconverting a feedstock including a plastic pyrolysis oil and/or solid recovered fuel pyrolysis oil fraction and a fossil-based hydrocarbon heavy fraction containing a portion of at least 50% by weight with a boiling point of at least 300° C. and containing sulfur and nitrogen, said pyrolysis oil fraction constituting less than 50% by weight of said feedstock, said process involving:

[0021] (a) conditioning and introducing said feedstock into a first hydroconversion section including at least a first ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor comprising a first porous supported hydroconversion catalyst; 5

[0022] (b) a first step of hydroconversion of said feedstock in the presence of hydrogen in said first hydroconversion section to obtain a first hydroconverted effluent;

[0023] (c) optionally, a step of separating part or all of said first effluent resulting from step (b), to form at least one heavy cut boiling predominantly at a temperature greater than or equal to 350° C.;

[0024] (d) optionally, a second hydroconversion step in a second hydroconversion section including at least a second ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor of part or all of said first effluent resulting from step (b) or optionally of said heavy cut resulting from step (c), said second hydroconversion reactor comprising a second porous supported catalyst and operating in the presence of hydrogen, to produce a second hydroconverted effluent;

[0025] step (b) and optional step (d) being performed at an absolute pressure of between 2 MPa and 38 MPa, at a temperature of between 300° C. and 550° C., at an

hourly space velocity of between 0.05 h^{-1} and 10 h^{-1} , and with an amount of hydrogen of between $50\text{ Nm}^3/\text{m}^3$ and $5000\text{ Nm}^3/\text{m}^3$,

[0026] (e) a step of fractionating all or some of said first hydroconverted effluent from step (b) or of said second hydroconverted effluent from step (d), in a fractionation section, to produce at least one heavy liquid product boiling predominantly at a temperature greater than or equal to 350°C ., said heavy liquid product containing a residual fraction boiling at a temperature greater than or equal to 540°C .

[0027] According to one or more implementations of the invention, in step (a), the pyrolysis oil fraction and the heavy hydrocarbon fraction of the feedstock are premixed before being introduced into said at least one first hydroconversion reactor of the first hydroconversion section.

[0028] According to one or more implementations of the invention, in step (a), the pyrolysis oil fraction and the heavy hydrocarbon fraction of the feedstock are introduced separately into said at least one first hydroconversion reactor of the first hydroconversion section.

[0029] According to one or more implementations of the invention, step (a) includes a step of preheating said heavy hydrocarbon fraction, preferably to a temperature of between 280°C . and 450°C ., and optionally a step of preheating the pyrolysis oil fraction, before the feedstock is introduced into the first hydroconversion reactor of the first hydroconversion section.

[0030] According to one or more implementations of the invention, the pyrolysis oil fraction constitutes between 1% and 45% by weight of the feedstock, preferably between 2% and 30% by weight of the feedstock, more preferentially between 2% and 25% by weight of the feedstock, and even more preferentially between 3% and 20% by weight of the feedstock.

[0031] According to one or more implementations of the invention, the feedstock is constituted of said of pyrolysis oil fraction and of said heavy hydrocarbon fraction, said pyrolysis oil fraction constituting between 1% and 45% by weight, preferably between 2% and 30% by weight, of said feedstock and the heavy hydrocarbon fraction constituting between 55% and 99% by weight, preferably between 70% and 98% by weight, of the feedstock.

[0032] According to one or more implementations of the invention, the pyrolysis oil fraction is a plastic pyrolysis oil.

[0033] According to one or more implementations of the invention, the heavy hydrocarbon fraction is chosen from the list consisting of a crude oil, a topped crude oil, an atmospheric residue or a vacuum residue resulting from the atmospheric and/or vacuum distillation of a crude oil or of an effluent originating from a thermal conversion, hydrotreating, hydrocracking or hydroconversion unit, an aromatic cut extracted from a unit for the production of lubricants, a deasphalted oil resulting from a deasphalting unit, an asphalt resulting from a deasphalting unit, a residual fraction resulting from direct coal liquefaction, a vacuum distillate resulting from direct coal liquefaction, or a mixture thereof.

[0034] According to one or more implementations of the invention, the heavy hydrocarbon fraction is a vacuum, preferably derived from the primary fractionation of a crude oil.

[0035] According to one or more implementations of the invention, the process includes separation step (c) which

separates part, or all, of the first hydroconverted effluent from step (b) to produce at least the heavy cut boiling predominantly at a temperature greater than or equal to 350°C ., and includes the second step (d) of hydroconverting said heavy cut.

[0036] According to one or more implementations of the invention, the hydroconversion reactor(s) of the first hydroconversion section in step (b), and optionally in hydroconversion step (d), are hybrid ebullated-entrained bed reactors, said process also including a step of introducing a catalyst precursor into the feedstock, said catalyst precursor preferably comprising molybdenum 2-ethylhexanoate, prior to injection of said feedstock into said at least one first ebullated-entrained hybrid bed reactor of the first hydroconversion section, in such a way that a colloidal or molecular catalyst, preferably including molybdenum disulfide, is formed when said feedstock reacts with sulfur.

[0037] According to one or more implementations of the invention, the first hydroconversion catalyst, and optionally the second hydroconversion catalyst, contains at least one non-noble group VIII metal chosen from nickel and cobalt, preferably nickel, and at least one group VIB metal chosen from molybdenum and tungsten, preferably molybdenum, and including an amorphous support, preferably alumina.

[0038] According to one or more embodiments of the invention, step (b) and the optional step (d) are performed at a temperature of between 405°C . and 450°C .

[0039] According to one or more implementations of the invention, the optional intermediate separation step (c) is performed in a separation section, and in which said separation section and/or the fractionation section in step (e) include means for washing at least one separated cut by contact with an aqueous solution.

[0040] According to one or more implementations of the invention, the process also comprises a step (f) of further processing the heavy liquid product and/or of the other product(s) from fractionation step (e), said step (f) comprising at least one step chosen from the list consisting of hydrotreating, steam cracking, fluid catalytic cracking, hydrocracking, deasphalting, lubricant oil extraction, and preferably a fixed-bed hydrotreatment step (f2) in a hydrotreatment section, said hydrotreatment section preferably comprising at least one fixed-bed reactor containing n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment section being fed with at least a portion of a liquid product from step (e) and a gaseous stream comprising hydrogen, to obtain a hydrotreated effluent.

[0041] According to a second aspect, the invention relates to a product obtained via the process according to the invention.

[0042] According to one or more implementations, the product is the hydroconverted effluent obtained on conclusion of the first hydroconversion step (b) or the second hydroconversion step (d), and includes a liquid part comprising, relative to the total weight of said liquid part of the effluent, a silicon content of less than or equal to 5 ppm by weight, and/or a chlorine element content of less than or equal to 10 ppm by weight.

[0043] Other subjects and advantages of the invention will become apparent on reading the description which follows of particular exemplary embodiments of the invention,

which are given as nonlimiting examples, the description being made with reference to the appended figures described below.

LIST OF FIGURES

[0044] FIG. 1 diagrammatically illustrates one embodiment of the hydroconversion process according to the invention.

[0045] FIG. 2 diagrammatically illustrates another embodiment of the hydroconversion process according to the invention.

[0046] In the figures, the same references denote identical or analogous elements.

DESCRIPTION OF THE EMBODIMENTS

[0047] Embodiments of the process according to the invention will now be described in detail. In the following detailed description, many specific details are disclosed in order to provide a deeper understanding of the process. However, it will be apparent to a person skilled in the art that the process can be performed without these specific details. In other cases, well-known characteristics have not been described in detail in order to avoid unnecessarily complicating the description.

[0048] A few definitions are given below for a better understanding of the invention.

[0049] In the present description, the term “to comprise” is synonymous with (means the same thing as) “to include” and “to contain”, and is inclusive or open-ended and does not exclude other elements which are not mentioned. It is understood that the term “to comprise” includes the exclusive and closed term “to consist of”.

[0050] In the present description, the expression “of between . . . and . . .” means that the limiting values of the interval are included in the described range of values, unless otherwise specified.

[0051] In the present invention, the different ranges of values of given parameters can be used alone or in combination. For example, a preferred range of pressure values can be combined with a more preferred range of temperature values, or a preferred range of values of one chemical compound or element can be combined with a more preferred range of values of another chemical compound or element.

[0052] The term “hydroconversion” refers to a process whose main aim is to reduce the boiling point range of a feedstock including at least 50% of a heavy hydrocarbon fraction with a boiling point of at least 300° C., or even of at least 450° C., and in which a substantial portion of the feedstock is converted into products having lower boiling point ranges than those of the starting feedstock. Hydroconversion generally involves the fragmentation of larger hydrocarbon molecules to give smaller molecular fragments having a smaller number of carbon atoms and a higher hydrogen to carbon ratio. The reactions performed during hydroconversion make it possible to reduce the size of hydrocarbon molecules, mainly by cleaving carbon-carbon bonds, in the presence of hydrogen in order to saturate the severed bonds and the aromatic rings. The mechanism by which hydroconversion takes place typically involves the formation of hydrocarbon free radicals during the fragmentation, mainly by thermal cracking, followed by the capping of the endings or fragments of free radicals with hydrogen

in the presence of active catalyst sites. Of course, during a hydroconversion process, other reactions typically associated with hydrotreating can take place, such as, inter alia, the removal of sulfur or nitrogen from the feedstock, or the saturation of olefins, and as defined more broadly below.

[0053] The term “hydrotreating”, commonly referred to as “HDT”, refers to a milder operation, the main aim of which is to remove impurities, such as sulfur, nitrogen, oxygen, halides and traces of metals, from the feedstock and to saturate olefins and/or to stabilize free radicals of hydrocarbons by reacting them with hydrogen rather than by leaving them to react with themselves. The main aim is not to change the boiling point range of the feedstock. Thus, hydrotreating notably comprises hydrodesulfurization (commonly known as “HDS”) reactions, hydrodenitrogenation (commonly known as “HDN”) reactions and hydrodemetallization (commonly known as “HDM”) reactions, accompanied by hydrogenation, hydrodeoxygenation (commonly known as “HDO”), hydrodearomatization, hydroisomerization, hydrodealkylation, hydrocracking or hydrodeasphalting reactions and by the reduction of Conradson carbon. Hydrotreating is most often performed using a fixed bed reactor, although other reactors can also be used for hydrotreating, for example an ebullated bed hydrotreating reactor.

[0054] The term “hydroconversion reactor” refers to any vessel in which the hydroconversion of a feedstock is the main aim, e.g. the cracking of the feedstock (that is to say, the reduction of the boiling point range), in the presence of hydrogen and of a hydroconversion catalyst. Hydroconversion reactors typically comprise at least one inlet orifice through which the feedstock and hydrogen can be introduced and an outlet orifice from which an upgraded material can be withdrawn. Specifically, hydroconversion reactors are also characterized in that they have sufficient thermal energy to bring about the fragmentation of larger hydrocarbon molecules to give smaller molecules by thermal decomposition. Examples of hydroconversion reactors comprise, without being limited thereto, entrained bed reactors, also called slurry reactors (reactors having three phases-liquid, gas, solid-in which the solid and liquid phases can behave as a homogeneous phase), ebullated bed reactors (fluidized reactors having three phases), moving bed reactors (reactors having three phases with downward movement of the solid catalyst and upward or downward flow of liquid and of gas) and fixed bed reactors (reactors having three phases with downward trickling of liquid feedstock onto a fixed bed of supported catalyst with hydrogen flowing typically simultaneously with the liquid, but possibly countercurrentwise in some cases).

[0055] The terms “hybrid bed” and “hybrid ebullated bed” and “hybrid ebullated-entrained bed” for a hydroconversion reactor refer to an ebullated-bed hydroconversion reactor comprising an entrained catalyst in addition to the porous supported catalyst maintained in the ebullated-bed reactor. In a similar manner, for a hydroconversion process, these terms thus refer to a process comprising hybrid operation of an ebullated bed and an entrained bed in at least one and the same hydroconversion reactor. The hybrid bed is a mixed bed of two types of catalyst 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 to as the “slurry catalyst”—being entrained out of the reactor with the effluent (upgraded feedstock). In the

present invention, the entrained catalyst is a colloidal catalyst or a molecular catalyst, as defined below.

[0056] The terms “colloidal catalyst” and “colloidally dispersed catalyst” refer to catalyst particles having a particle size that is colloidal, 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” comprises, but is not limited to, molecular or molecularly dispersed catalyst compounds.

[0057] The terms “molecular catalyst” and “molecularly dispersed catalyst” refer to catalyst compounds which are essentially “dissolved” or completely dissociated from other catalyst compounds or molecules in a feedstock, nonvolatile liquid fraction, bottom fraction, residue, or other feedstock or product in which the catalyst may be found. They also refer to very small catalyst particles or sheets which contain only a few catalyst molecules joined together (e.g. 15 molecules or less).

[0058] The terms “porous supported catalyst”, “solid supported catalyst” and “supported catalyst” refer to catalysts which 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 cobalt, nickel, tungsten or molybdenum sulfides, or mixed sulfides of these elements (for example NiMo, CoMo, and the like), which are dispersed in the pores. Supported catalysts are commonly produced in the form of cylindrical extrudates (pellets) or of spherical solids, although other forms are possible.

[0059] In the text hereinbelow, the term “pyrolysis oil” means an oil obtained from the pyrolysis of plastics and/or SRFs, unless otherwise indicated. Also for the sake of simplicity, the term “heavy hydrocarbon fraction” of the feedstock denotes a fossil-based heavy hydrocarbon fraction, unless otherwise indicated.

[0060] The process according to the invention and the functioning thereof are described in greater detail below, notably with reference to FIGS. 1 and 2 which are diagrammatic representations of exemplary embodiments of the process according to the invention, for a better understanding of the invention, without however the invention being limited to these examples.

[0061] The object of the invention is to propose a process for the hydroconversion of a feedstock including a plastic and/or SRF pyrolysis oil fraction **102** and a fossil-based heavy hydrocarbon fraction **101** containing a portion of at least 50% by weight with a boiling point of at least 300° C. and containing sulfur and nitrogen, said pyrolysis oil fraction constituting less than 50% by weight of said feedstock, the process involving the following steps:

[0062] (a) conditioning and introducing said feedstock into a first hydroconversion section **20** including at least a first ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor comprising a first porous supported hydroconversion catalyst;

[0063] (b) a first step of hydroconversion of said feedstock in the presence of hydrogen in said first hydroconversion section to obtain a first hydroconverted effluent;

[0064] (c) optionally, a step of separating part or all of said first effluent resulting from step (b), to form at least one heavy cut boiling predominantly at a temperature greater than or equal to 350° C.;

[0065] (d) optionally, a second hydroconversion step in a second hydroconversion section including at least a second ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor of part or all of said first effluent resulting from step (b) or optionally of said heavy cut resulting from step (c), said second hydroconversion reactor comprising a second porous supported catalyst and operating in the presence of hydrogen, to produce a second hydroconverted effluent;

[0066] step (b) and optional step (d) being performed at an absolute pressure of between 2 MPa and 38 MPa, at a temperature of between 300° C. and 550° C., at an hourly space velocity of between 0.05 h^{-1} and 10 h^{-1} , and with an amount of hydrogen of between 50 Nm^3/m^3 and 5000 Nm^3/m^3 ,

[0067] (e) a step of fractionating all or some of said first hydroconverted effluent from step (b) or of said second hydroconverted effluent from step (d), in a fractionation section **30**, to produce at least one heavy liquid product which boils predominantly at a temperature greater than or equal to 350° C., said heavy liquid product containing a residual fraction boiling at a temperature greater than or equal to 540° C.

The Feedstock

[0068] According to an essential aspect of the invention, the feedstock predominantly comprises a fossil-based heavy hydrocarbon fraction and a minor fraction of plastic pyrolysis oil and/or SRF pyrolysis oil.

[0069] According to a preferred embodiment of the invention, the feedstock is constituted of said minor fraction of plastic pyrolysis oil and/or SRF pyrolysis oil and of a fossil-based heavy hydrocarbon fraction.

[0070] The process according to the invention is thus specific to the hydroconversion of a mixture of plastic pyrolysis oil and/or SRF pyrolysis oil at low content and of a fossil-based heavy hydrocarbon fraction.

[0071] The fraction of plastic pyrolysis oil and/or SRF pyrolysis oil constitutes less than 50% by weight of the feedstock (total weight of the feedstock), preferably between 1% and 45% by weight of the feedstock, more preferentially between 2% and 30% by weight of the feedstock, even more preferentially between 2% and 25% by weight of the feedstock, even more preferentially between 3% and 20% by weight of the feedstock and even more preferably between 5% and 20% by weight of the feedstock, or even between 5% and 15% by weight of the feedstock.

[0072] The feedstock can be constituted of these two fractions alone: the pyrolysis oil fraction and the heavy hydrocarbon fraction, the sum of the pyrolysis oil fraction and of the heavy hydrocarbon fraction forming 100% by weight of the feedstock. The heavy hydrocarbon fraction can constitute, preferably when the feedstock is constituted of said heavy hydrocarbon fraction and of the pyrolysis oil fraction, between 55% and 99% by weight of the feedstock, preferably between 70% and 98% by weight of the feed-

stock, more preferentially between 75% and 98% by weight of the feedstock, even more preferentially between 80% and 97% by weight of the feedstock and in an even more preferred manner between 80% and 95% by weight of the feedstock, or even between 85% and 95% by weight of the feedstock.

[0073] According to the invention, a “plastic pyrolysis oil or SRF pyrolysis oil” is an oil, advantageously in liquid form at room temperature, obtained from the pyrolysis of plastics, preferably of plastic waste notably originating from collection and sorting channels, or originating from the pyrolysis of SRFs. It comprises in particular a mixture of hydrocarbon compounds, notably paraffins, olefins, naphthenes and aromatics. At least 80% by weight of these hydrocarbon compounds preferably have a boiling point of less than 700° C., and preferably less than 550° C. In particular, depending on the origin of the pyrolysis oil, said oil may comprise up to 70% by weight of paraffins, up to 90% by weight of olefins and up to 90% by weight of aromatics, it being understood that the sum of the paraffins, of the olefins and of the aromatics is equal to 100% by weight of the hydrocarbon compounds.

[0074] The density of the pyrolysis oil, measured at 15° C. according to the ASTM D4052 method, is generally of between 0.75 g/cm³ and 0.99 g/cm³, preferably of between 0.75 g/cm³ and 0.95 g/cm³.

[0075] The pyrolysis oil may comprise, and usually does comprise, impurities, such as metals, notably iron, silicon or halogenated compounds, notably chlorinated compounds. These impurities may be present in the pyrolysis oil in high contents, for example up to 500 ppm by weight or even 1000 ppm by weight or even 5000 ppm by weight of halogen elements (e.g. chlorine) provided by halogenated compounds (e.g. chlorinated compounds), up to 2500 ppm by weight, or even 10 000 ppm by weight of metallic or semi-metallic elements. Alkali metals, alkaline-earth metals, transition metals, post-transition metals and metalloids may be likened to contaminants of metallic nature, referred to as metals or metallic or semi-metallic elements. The pyrolysis oil may comprise up to 200 ppm by weight or even 1000 ppm by weight of silicon, and up to 15 ppm by weight or even 100 ppm by weight of iron. The pyrolysis oil may also comprise other impurities such as heteroelements notably provided by sulfur compounds, oxygen compounds and/or nitrogen compounds, in contents generally less than 20 000 ppm by weight of heteroelements and preferably less than 10 000 ppm by weight of heteroelements.

[0076] The process according to the invention is particularly suitable for treating a pyrolysis oil laden with impurities, in combination with a heavy hydrocarbon feedstock as is defined in greater detail hereinbelow. The term “laden with impurities” means that the pyrolysis oil has the following properties:

[0077] a content of aromatic compounds of between 0 and 90% by weight, often between 20% and 90% by weight, and which may be between 50% and 90% by weight;

[0078] a content of halogenated compounds of between 2 ppm by weight and 5000 ppm by weight, often between 200 ppm by weight and 5000 ppm by weight, and which may be between 500 ppm by weight and 5000 ppm by weight;

[0079] a content of metal elements of between 10 ppm by weight and 10 000 ppm by weight, often between

2000 ppm by weight and 10 000 ppm by weight, and which may be between 2250 ppm by weight and 5000 ppm by weight;

[0080] including a content of iron element of between 0 ppm by weight and 100 ppm by weight, often between 10 ppm by weight and 100 ppm by weight, and which may be between 15 ppm by weight and 100 ppm by weight;

[0081] a content of silicon element of between 0 ppm by weight and 1000 ppm by weight, often between 50 ppm by weight and 1000 ppm by weight, or even between 80 ppm by weight or 100 ppm by weight and 1000 ppm by weight, and which may also be between 200 ppm by weight and 1000 ppm by weight.

[0082] The process according to the invention is particularly suitable for treating a pyrolysis oil highly laden with impurities, in combination with a heavy hydrocarbon feedstock as defined in greater detail hereinbelow. The term “highly laden with impurities” means that the pyrolysis oil has the following properties:

[0083] a content of aromatic compounds of between 350% and 70% by weight;

[0084] a content of halogenated compounds of between 500 ppm by weight and 5000 ppm by weight;

[0085] a content of metal elements of between 300 ppm by weight and 5000 ppm by weight;

[0086] including a content of iron element of between 15 ppm by weight and 100 ppm by weight;

[0087] a content of silicon element of between 200 ppm by weight and 1000 ppm by weight.

[0088] The SRF and/or plastic pyrolysis oil may be obtained from a thermal or catalytic pyrolysis treatment or else may be prepared by hydropyrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

[0089] The fossil-based heavy hydrocarbon fraction of the feedstock of the process according to the invention is a heavy hydrocarbon fraction containing a portion of at least 50% by weight, preferably at least 80% by weight, having a boiling point of at least 300° C., preferably at least 350° C., and even more preferably at least 375° C.

[0090] This heavy hydrocarbon fraction of the feedstock may be a crude oil, or originate from the refining of a crude oil or the processing of another fossil hydrocarbon source in a refinery.

[0091] The heavy hydrocarbon fraction of the feedstock may be a crude oil, a topped crude oil or may comprise, or be constituted of, atmospheric residues and/or vacuum residues from the atmospheric and/or vacuum distillation of a crude oil.

[0092] The heavy hydrocarbon fraction of the feedstock can also be constituted of atmospheric and/or vacuum residues resulting from the atmospheric and/or vacuum distillation of effluents originating from thermal conversion, hydrotreating, hydrocracking and/or hydroconversion units.

[0093] Preferably, the heavy hydrocarbon fraction of the feedstock is a heavy hydrocarbon fraction containing a portion of at least 50% by weight, or even at least 80% by weight, having a boiling point of at least 450° C., preferably of at least 500° C., and even more preferably of at least 540° C., such as a vacuum residue.

[0094] Advantageously, the heavy hydrocarbon fraction of the feedstock is constituted of one or more vacuum residues. The vacuum residues can come directly from crude oil, or from other refining units, such as, inter alia, the hydrotreat-

ing of residues, the hydrocracking of residues or the vis-breaking of residues. Preferably, the vacuum residues are vacuum residues from the vacuum distillation column of the primary (straight-run (SR)) fractionation of crude oil.

[0095] The heavy hydrocarbon fraction of the feedstock may also be constituted of aromatic cuts extracted from a lubricant production unit, deasphalted oils from a deasphalting unit, also known as DAO (deasphalting unit raffinates), asphalts from a deasphalting unit (deasphalting unit residues).

[0096] The heavy hydrocarbon fraction of the feedstock may also be constituted of a settling oil or a recycle oil (which typically has a boiling range from 360° C. to 550° C.), for example an FCC fluidized bed catalytic cracking effluent such as a heavy cycle oil (HCO) or a slurry oil (SLO).

[0097] The heavy hydrocarbon fraction of the feedstock may also be a residual fraction from direct coal liquefaction (an atmospheric residue and/or a vacuum residue from the H-Coal® process, for example), or a vacuum distillate from direct coal liquefaction, for instance the H-Coal® process.

[0098] All these fractions of fossil origin can be used to constitute the heavy hydrocarbon fraction of the feedstock treated according to the invention, alone or as a mixture.

[0099] According to one or more implementations, the heavy hydrocarbon fraction comprises, and may be constituted of, at least one of the following feedstocks, alone or as mixtures: a crude oil, a topped crude oil, an atmospheric residue or a vacuum residue from the atmospheric or vacuum distillation of a crude oil (preferably from the primary fractionation of crude oil), an atmospheric residue or a vacuum residue from atmospheric or vacuum distillation obtained via a direct coal liquefaction process, and preferably is a vacuum residue from the vacuum distillation of a crude oil (preferably from the primary fractionation of crude oil).

[0100] The heavy hydrocarbon fraction of the feedstock treated according to the invention contains impurities, such as sulfur and nitrogen. It may also contain impurities such as metals, Conradson carbon and asphaltenes, in particular C₇ asphaltenes which are insoluble in heptane.

[0101] The metal contents may be greater than or equal to 20 ppm by weight, preferably greater than or equal to 100 ppm by weight.

[0102] The sulfur content may be greater than or equal to 0.1% by weight, or even greater than or equal to 0.5% or 1% by weight, and may be greater than or equal to 2% by weight.

[0103] The nitrogen content is usually between 1 ppm and 8000 ppm by weight, more generally between 200 ppm and 8000 ppm by weight, for example between 2000 ppm and 8000 ppm by weight.

[0104] The content of C₇ asphaltenes (compounds that are insoluble in heptane according to the standard ASTM D6560, also corresponding to the standard NF T60-115) can amount to a minimum of 1% by weight and is often greater than or equal to 3% by weight (with the exception of a heavy hydrocarbon fraction essentially including a DAO). 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 which severely limit the operability of hydrotreating and hydroconversion units.

[0105] The Conradson carbon content may be greater than or equal to 3% by weight, or even at least 5% by weight. The content of Conradson carbon is defined by the standard ASTM D482 and represents, for a person skilled in the art, a well-known evaluation of the amount of carbon residues produced after pyrolysis under standard temperature and pressure conditions.

[0106] These contents of metals, sulfur, nitrogen, asphaltenes and Conradson carbon of the heavy hydrocarbon fraction are expressed as % by weight of the total weight of the heavy hydrocarbon fraction of the feedstock.

[0107] According to one or more implementations, the feedstock of the process according to the invention may also comprise, at a low content, typically between 1% and 20% by weight of the feedstock, or even between 1% and 10% or 5% by weight, a plant and/or animal oil or fat fraction, and/or a hydrocarbon fraction resulting from processes for the thermal and/or catalytic conversion of lignocellulosic biomass, such as an oil produced from lignocellulosic biomass, according to various liquefaction methods, such as hydrothermal liquefaction or pyrolysis, which is then co-treated with the plastic pyrolysis oil and/or SRF pyrolysis oil and the fossil-based heavy hydrocarbon fraction.

[0108] Oils/fats of plant and/or animal origin contain triglycerides and/or free fatty acids and/or esters. The plant oils may advantageously be crude or completely or partially refined, and may result from the following plants: rape, sunflower, soya, palm, palm kernel, olive, coconut, jatropha (French physic nut), castor oil plant, cotton, groundnut, flax or sea kale, this list not being limiting. Algal oils or fish oils are also relevant. The oils/fats of plant and/or animal origin can be waste oils/fats, for example waste cooking oils. The animal fats can be chosen from pig fat or fats composed of residues from the food industry or resulting from the catering industries.

[0109] The term “lignocellulosic biomass” denotes compounds derived from plants or from their by-products, and comprises constituents chosen from the group formed by cellulose, hemicellulose (carbohydrate polymers) and/or lignin (aromatic polymer).

[0110] According to one or more implementations, the feedstock of the process according to the invention does not include a plant and/or animal oil or fat fraction, or a hydrocarbon fraction resulting from processes for the thermal and/or catalytic conversion of lignocellulosic biomass, such as a biomass pyrolysis oil.

(a) Step of Conditioning and Injecting the Feedstock into the First Hydroconversion Reactor

[0111] The process according to the invention comprises a step (a) of conditioning and introducing the feedstock into a first hydroconversion section 20 including at least a first ebullated bed or hybrid bed reactor comprising a first porous supported hydroconversion catalyst.

[0112] The term “conditioning of the feedstock” means putting said feedstock in a state suitable for hydroconversion step b), notably putting it under temperature and pressure conditions suitable for hydroconversion in the first hydroconversion reactor, optional mixing of the plastic pyrolysis oil and/or SRF pyrolysis oil fractions and heavy hydrocarbon fraction before the introduction of the feedstock into the reactor, and possible removal of solid particles from the plastic pyrolysis oil and/or SRF pyrolysis oil fraction (by filtration, centrifugation, electrostatic separation, washing with an aqueous solution, adsorption, etc.).

[0113] Specifically, the plastic pyrolysis oil and/or SRF pyrolysis oil fraction **102** can be mixed beforehand with the heavy hydrocarbon fraction **101** of the feedstock before entering the first hydroconversion reactor in the first hydroconversion step (b). In this case, the two fractions may be heated beforehand to ensure that they are in the liquid state before being mixed, by means of any heating device known to those skilled in the art. Alternatively, only the heavy hydrocarbon fraction **101** can be heated, notably if the pyrolysis oil fraction is liquid and pumpable at ambient temperature. This mixing may be performed in a dedicated vessel **10** as represented in FIG. 1, it being possible for the mixing to be optionally active (e.g. a pump with an impeller rotor or propeller), or directly by the connection of the two conduits transporting the products. In the latter case, the homogeneity of the mixture can be ensured by the installation of an in-line static mixer, this technology being well known to those skilled in the art.

[0114] By mixing fractions, a more homogeneous feedstock **114** is introduced into the first hydroconversion reactor, this being, for example, favorable to good fluidization of the catalyst, and to good hydrodynamic functioning of the reactor in general. It may also allow the use of common equipment, such as ovens, feedstock distributors, mixers for mixing hydrogen with the feedstock, for example of the T-mixer type, which can contribute toward reducing the investment costs.

[0115] Another possibility, shown in FIG. 2, is the separate injection of the plastic pyrolysis oil and/or SRF pyrolysis oil fraction **102** and of the heavy hydrocarbon fraction **101** into the first hydroconversion reactor in the first hydroconversion step (b). This injection mode may be preferred in order to avoid any problem related to a chemical incompatibility between the two fractions (risk of phase separation or of precipitation of asphaltenes, for example), or also in order to prevent possible accelerated fouling of the preheating oven (the high contents of diolefins and olefins of the plastic pyrolysis oil and/or SRF pyrolysis oil can result in the formation of gums).

[0116] According to these two alternative embodiments, i.e. mixing or not mixing the fractions before their introduction into the first hydroconversion reactor, the feedstock, and in particular the heavy hydrocarbon fraction **101** of the feedstock, is heated to a temperature suitable for the hydroconversion in the first hydroconversion reactor, that is to say so as to advantageously reach a target temperature in the first hydroconversion reactor. This will be referred to in the present description as a preheating step. It is pointed out that said target temperature in the hydroconversion reactor, i.e. the temperature during the hydroconversion step, is generally not the preheating temperature, the latter being conventionally lower than the target temperature in the hydroconversion reactor.

[0117] The preheating of the heavy hydrocarbon fraction is preferably performed at a temperature of between 280° C. and 450° C., even more preferably between 300° C. and 400° C. and even more preferably between 320° C. and 365° C.

[0118] This preheating may also involve heating the pyrolysis oil fraction **102**, notably if said fraction is injected separately from the fraction **101** into the first hydroconversion reactor; however, preferably at a lower temperature than for the heavy hydrocarbon fraction **101**. Advantageously, the pyrolysis oil fraction **102**, when injected into

the first reactor separately from the heavy hydrocarbon fraction **101**, may be heated to a temperature between room temperature, e.g. 15° C., and 350° C., preferably between 100° and 350° C., more preferentially between 100° C. and 250° C., even more preferentially between 100° C. and less than 230° C., or even between 150° C. and less than 200° C.

[0119] In the case of a mixture of the two fractions, the preheating can be performed after, before or during the mixing.

[0120] According to one embodiment in which preheating is performed separately for fractions **101** and **102**, and in which fractions **101** and **102** are then mixed, the plastic pyrolysis oil and/or SRF pyrolysis oil fraction **102** is preheated to a lower temperature than the heavy hydrocarbon fraction **101**, so as to limit gum formation and/or coking of the preheating equipment (for example furnaces and/or heat exchangers) due to the presence of olefins and diolefins in the pyrolysis oil fraction **102**. According to this embodiment, the preheating temperature of the plastic pyrolysis oil and/or SRF pyrolysis oil fraction **102** is preferably less than 230° C., preferably less than 200° C., more preferentially less than or equal to 175° C., and very preferably less than or equal to 100° C. According to this embodiment, the heavy fraction **101** may be preheated, prior to mixing with the pyrolysis oil fraction **102**, to a temperature of between 280° C. and 450° C., even more preferably between 300° C. and 400° C., and even more preferably between 320° C. and 365° C.

[0121] According to another embodiment in which the heavy hydrocarbon fraction **101** and the pyrolysis oil fraction **102** are mixed, the pyrolysis oil fraction **102** is indirectly heated by mixing it with the heavy hydrocarbon fraction **101** (i.e. heat exchange between the two fractions by placing said two fractions which have different temperatures in contact), which has been preheated preferably to between 280° C. and 450° C., even more preferably to between 300° C. and 400° C., and even more preferably to between 320° C. and 365° C., in such a way that a target hydroconversion temperature can then be reached in the first hydroconversion reactor.

[0122] According to yet another embodiment, it is the mixture of the heavy hydrocarbon fraction **101** and the pyrolysis oil fraction **102** that is preheated, advantageously using heating means as already described below (e.g.: furnace, heat exchangers, etc.), preferably to between 280° C. and 450° C., even more preferably to between 300° C. and 400° C., and even more preferably to between 320° C. and 365° C., so that a target hydroconversion temperature can then be reached in the first hydroconversion reactor.

[0123] According to one embodiment, preheating may also comprise heat exchange between the feedstock and a stream including preheated hydrogen (not shown in the figures), typically having a temperature of between 350° C. and 560° C., for example about 500° C. or 540° C., so that a target hydroconversion temperature can then be reached in the first hydroconversion reactor.

[0124] Any means known to a person skilled in the art that is capable of preheating said feedstock can be used. Use may be made of at least one oven, commonly known as a preheating oven, comprising, for example, at least one heating compartment, and/or tubes in which the feedstock flows, a mixer for mixing the feedstock with H₂, heat

exchangers of any appropriate type, for example tubular or spiral heat exchangers in which the feedstock flows, and the like.

[0125] Before it is introduced into the first hydroconversion reactor, the feedstock is subjected to a pressurization step in order to be suited to the pressure prevailing in the first hydroconversion reactor, for example by means of a suitable pump. This pressurization step is preferably performed before the preheating step.

[0126] According to one or more embodiments, the plastic pyrolysis oil and/or SRF pyrolysis oil fraction **102** may first undergo a filtration step and/or a centrifugation step and/or an electrostatic separation step and/or a washing step using an aqueous solution and/or an adsorption step, to remove impurities which may be naturally present in plastic pyrolysis oils and/or SRF pyrolysis oils, notably to remove solid particles.

[0127] Prior to its introduction into the first hydroconversion reactor, the feedstock may be mixed with an entrained catalyst precursor **104**, for example the heavy hydrocarbon fraction **101** may be mixed with an entrained catalyst precursor **104**, as represented in FIGS. 1 and 2, so that, when an entrained catalyst is formed, notably by reaction with sulfur, the entrained catalyst will comprise a colloidal or molecular catalyst dispersed in the feedstock.

[0128] The entrained catalyst precursor **104** may also be mixed with the pyrolysis oil fraction **102** before mixing the latter with the heavy hydrocarbon fraction **101** (not represented in FIG. 1), or may be mixed with the feedstock **114** formed by the mixing of said fractions **101** and **102** (not represented in FIG. 2), in the same manner as described below for a mixture between the heavy hydrocarbon fraction **101** and the entrained catalyst precursor **104**, with the exception of the temperature for mixing the catalyst precursor with the pyrolysis oil fraction **102** which is preferably less than 230° C., or even less than 200° C. (and in any case preferably at a temperature below a temperature at which a substantial part of the catalyst precursor begins to decompose).

[0129] It is specified that, for the purposes of the present invention, the catalyst precursor, optionally diluted, does not form part of the feedstock as defined above, which includes the plastic pyrolysis oil and/or SRF pyrolysis oil fraction and the heavy hydrocarbon fraction.

[0130] The entrained catalyst precursor may be chosen from any metal catalyst precursor known to those skilled in the art, which is capable of forming a colloidal or molecularly dispersed catalyst (i.e. the entrained catalyst) in the presence of hydrogen and/or H₂S and/or any other source of sulfur, and which allows hydroconversion of the feedstock after injection into the first hydroconversion reactor. The catalyst precursor is advantageously an oil-soluble catalyst precursor containing at least one transition metal.

[0131] The catalyst precursor preferably comprises an oil-soluble organometallic compound or complex.

[0132] The catalyst precursor may comprise an oil-soluble organometallic or bimetallic compound or complex comprising one or two of the following metals: Mo, Ni, V, Fe, Co or W, or mixtures of such compounds/complexes.

[0133] The oil-soluble catalyst precursor preferably has a decomposition temperature (temperature below which the catalyst precursor is substantially chemically stable) in a

range from 100° C. to 350° C., more preferably in a range from 150° C. to 300° C., and most preferably in a range from 175° C. to 250° C.

[0134] The oil-soluble organometallic compound or complex is preferably chosen from the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate, vanadium naphthanate, vanadium octoate, molybdenum hexacarbonyl, vanadium hexacarbonyl, and iron pentacarbonyl. These compounds are nonlimiting examples of oil-soluble catalyst precursors.

[0135] More preferably, the catalyst precursor comprises Mo and, for example, comprises a compound chosen from the group consisting of molybdenum 2-ethylhexanoate, molybdenum naphthanate and molybdenum hexacarbonyl.

[0136] A currently preferred catalyst precursor 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 sufficiently high decomposition temperature or decomposition temperature range to avoid substantial thermal decomposition when mixed with a heavy hydrocarbon fraction at a temperature below 250° C.

[0137] A person skilled in the art may choose a mixing temperature profile that results in mixing of the chosen precursor without substantial thermal decomposition prior to colloidal or molecular catalyst formation.

[0138] Catalyst precursor **104**, preferably an oil-soluble catalyst precursor, may be premixed with a hydrocarbon stream of diluent to form a dilute precursor mixture, as described in US2005/0241991, U.S. Pat. No. 10,822,553 or U.S. Pat. No. 10,941,353 and recalled below.

[0139] Catalyst precursor **104** may be premixed with a diluent to form a diluted precursor mixture, said premixing preferably being performed at a temperature below a temperature at which a substantial portion of the catalyst precursor begins to decompose, preferably between ambient temperature, e.g. 15° C., and 300° C., more preferably between 15° C. and 200° C., even more preferably between 50° C. and 200° C., even more preferably between 75° C. and 150° C., and even more preferably between 75° C. and 100° C., and advantageously for a period of time from 1 second to 30 minutes.

[0140] Typically, the catalyst precursor diluent may be a hydrocarbon-based oil composed of hydrocarbons of which at least 50% by weight, relative to the total weight of the hydrocarbon-based oil, have a boiling point of between 180° C. and 540° C. Examples of hydrocarbon-based diluents that are suitable for precursor dilution include, but are not limited to, vacuum gas oil known as "VGO" (which typically has a boiling range of 360° C. to 524° C.), settling oil or recycle oil (which typically has a boiling range of 360° C. to 550° C.), for example, FCC fluidized-bed catalytic cracking effluent, such as heavy cycle oil (HCO) or light cycle oil (LCO), pyrolysis oil from a hydrocracker, light gas oil (which typically has a boiling range of 200° C. to 360° C.), atmospheric residues, vacuum residues (which typically have a boiling range of greater than or equal to 524° C.), deasphalted oils, and resins. The catalyst precursor diluent is preferably atmospheric residue, vacuum residue or VGO.

[0141] Next, the diluted precursor can be mixed with the heavy hydrocarbon fraction **101**, preferably at a temperature between ambient temperature, e.g. 15° C., and 300° C., and advantageously for a period of time of from 1 second to 30 minutes, preferably from 1 second to 10 minutes, and even

more preferably within a range of from 2 seconds to 3 minutes. In the present description, a mixing time (or residence time for mixing) of 1 second means instantaneous mixing.

[0142] The mass ratio of catalyst precursor **104** to hydrocarbon oil diluent is preferably within a range of about 1:500 to approximately 1:1, more preferably within a range of about 1:150 to approximately 1:2, and even more preferably within a range of about 1:100 to approximately 1:5 (e.g. 1:100, 1:50, 1:30, or 1:10).

[0143] Without mixing with a diluent, it is preferable to ensure that the components are mixed for a sufficient time to completely/intimately mix the catalyst precursor into the heavy hydrocarbon fraction before the entrained catalyst is formed. However, a long mixing time, for example 24 hours, may be prohibitively expensive for certain industrial operations.

[0144] Premixing the catalyst precursor **104** with a hydrocarbon-based diluent greatly facilitates thorough and intimate mixing of the precursor into the heavy hydrocarbon fraction, particularly in the relatively short period of time required for large-scale industrial operations to be economically viable.

[0145] The diluted precursor is preferably combined with the heavy hydrocarbon fraction and mixed for a sufficient time and in such a manner as to disperse the catalyst precursor throughout the heavy fraction so that the catalyst precursor is completely/intimately mixed with the heavy hydrocarbon fraction. In order to obtain sufficient mixing prior to colloidal or molecular catalyst formation, the diluted precursor and the heavy fraction are more preferably mixed for a period of time in the range from 1 second to 10 minutes, and even more preferably in the range from 2 seconds to 3 minutes.

[0146] Increasing the vigor and/or shear energy of the mixing process generally reduces the time required to achieve complete/intimate mixture. Examples of mixing appliances that may be used for performing complete/intimate mixing of catalyst precursor **104** and heavy hydrocarbon feedstock **101** comprise, without being limited thereto, high shear mixing, such as a mixture created in a pump with an impeller rotor or propeller, multiple static in-line mixers, multiple static in-line mixers in combination with high shear in-line mixers, multiple static in-line mixers in combination with high shear in-line mixers followed by recirculation pumping in the holding tank, combinations of the above appliances followed by one or more multi-stage centrifugal pumps.

[0147] The heavy hydrocarbon fraction **101** and the diluted precursor are preferably mixed and conditioned at a temperature within a range of from 50° C. to 200° C., more preferably within a range of from 75° C. to 175° C. Preferably, the gauge pressure is between 0 MPa and 25 MPa, more preferably between 0.01 MPa and 5 MPa.

[0148] Under the operating conditions of the hydroconversion reactor in hydroconversion step (b), the catalyst precursor **104** is totally decomposed and the precursor metal has combined with sulfur (e.g. dissolved H₂S present in the feedstock, or H₂S contained in hydrogen recycled to the hydroconversion reactor, or sulfur from organic sulfur molecules present in the feedstock or possibly previously introduced into the feedstock) to give the colloidal or molecular catalyst.

[0149] The metal concentration of the catalyst, preferably Mo, in the feedstock is preferably between 5 ppm and 500 ppm by weight of the feedstock, more preferably between 10 ppm and 300 ppm by weight, more preferably between 10 ppm and 175 ppm by weight, even more preferably between 10 ppm and 75 ppm by weight, and even more preferably between 10 ppm and 50 ppm by weight.

[0150] Preferably, the colloidal or molecular catalyst comprises, or is constituted of, molybdenum disulfide.

[0151] As described above, the pyrolysis oil fraction **102** is introduced, mixed or not with the heavy hydrocarbon fraction **101**, into the first hydroconversion reactor of the first hydroconversion section **20**. However, the first hydroconversion step may comprise several hydroconversion reactors in series, and the pyrolysis oil fraction **102** may be placed in a hydroconversion reactor downstream of the first hydroconversion reactor of the first hydroconversion section **20** without departing from the context of the present invention.

(b) First Hydroconversion Step

[0152] The feedstock is introduced, regardless of whether the fractions of which it is composed are separated (**101** and **102**) or mixed (**114**) according to step (a), into the first hydroconversion reactor of the first hydroconversion section **20**, together with hydrogen (stream not represented). Said first reactor comprises a first porous supported hydroconversion catalyst.

[0153] The first hydroconversion step (b) is performed under conditions affording a first hydroconverted effluent **105**. Said first hydroconverted effluent **105** contains the conversion products; notably, said first effluent has a reduced content (relative to the feedstock) of hydrocarbons having a boiling point of at least 300° C., or of at least 350° C., 375° C., 450° C., 500° C., or even 540° C. depending on the nature of the feedstock. Said first hydroconverted effluent **105** may also have a reduced content, relative to the feedstock, of sulfur, and/or of metals, and/or of silicon, and/or of halogenated compounds (e.g. chlorine), and/or of nitrogen, and/or of Conradson carbon, and/or of asphaltenes, depending on the reactions performed in the first hydroconversion reactor and the composition of the feedstock. In particular, said first hydroconverted effluent **105** may advantageously have a reduced content, relative to the feedstock, of sulfur, metals, silicon, halogenated compounds (e.g. chlorine), nitrogen, Conradson carbon and asphaltenes.

[0154] The content of silicon and/or halogenated compounds (e.g. chlorine) in the first hydroconverted effluent **105** obtained on conclusion of step b) is advantageously reduced relative to the content of the same impurities (i.e. silicon and/or halogenated compounds such as chlorine) in the feedstock. Preferably, the first hydroconverted effluent **105** includes a liquid fraction (PI+ fraction) having:

[0155] a silicon content of less than or equal to 5 ppm by weight, preferably less than or equal to 2 ppm by weight, or even less than or equal to 1 ppm by weight relative to the total weight of said liquid part of the first hydroconverted effluent **105**, and/or

[0156] a content of chlorine element of less than or equal to 10 ppm by weight, preferably less than or equal to 5 ppm by weight, or even less than or equal to 2 ppm by weight or even 1 ppm by weight, relative to the total weight of said liquid part of the first hydroconverted effluent **105**.

[0157] Step (b) is preferably performed at an absolute pressure of between 2 MPa and 38 MPa, more preferentially between 5 MPa and 25 MPa, and even more preferably between 6 MPa and 20 MPa, at a temperature of between 300° C. and 550° C., more preferentially between 350° C. and 500° C., preferably between 370° C. and 450° C., and even more preferentially between 405° C. and 450° C., or even between 410° C. and 450° C.

[0158] The hourly space velocity (HSV) (HSV relative to the volume of each reactor) is preferably between 0.05 h⁻¹ and 10 h⁻¹. The hourly space velocity (HSV), also referred to as the liquid hourly space velocity (LHSV), is defined here as the ratio between the hourly volumetric flow rate of the liquid feedstock (sent to the hydroconversion step) and the volume of each hydroconversion reactor. According to a preferred implementation, the HSV is between 0.1 h⁻¹ and 10 h⁻¹, more preferentially between 0.1 h⁻¹ and 5 h⁻¹, even more preferably between 0.15 h⁻¹ and 2 h⁻¹, and even more preferably between 0.15 h⁻¹ and 1 h⁻¹.

[0159] According to another implementation, the overall HSV, that is to say the flow rate of liquid feedstock sent to step b) in relation to the volume of all the reactors if several hydroconversion reactors are used in step b), is between 0.05 h⁻¹ and 0.09 h⁻¹.

[0160] The amount of hydrogen mixed with the feedstock is preferably between 50 and 5000 normal cubic meters (Nm³) per cubic meter (m³) of liquid feedstock, preferably between 100 Nm³/m³ and 2000 Nm³/m³ and very preferably between 200 Nm³/m³ and 1000 Nm³/m³.

[0161] The first hydroconversion section 20 includes one or more ebullated or hybrid bed reactors, containing at least one first supported hydroconversion catalyst, the reactors possibly being arranged in series and/or in parallel. In this step, at least one first supported hydroconversion catalyst is thus maintained in the reactor(s). According to one or more embodiments of the invention, the first hydroconversion section 20 comprises one or more hydroconversion reactors, which may be in series and/or in parallel, operating as an ebullated bed, as used for the H-Oil® process, as described, for example, in patents U.S. Pat. No. 4,521,295 or U.S. Pat. No. 4,495,060 or U.S. Pat. No. 4,457,831 or U.S. Pat. No. 4,354,852, in the article Aiche, Mar. 19-23, 1995, Houston, Texas, article number 46d, "Second generation ebullated bed technology", or in chapter 3.5, "Hydroprocessing and Hydroconversion of Residue Fractions", of the book "Catalysis by Transition Metal Sulphides", published by Technip in 2013. According to this or these embodiments, each reactor is operated as a fluidized bed known as an ebullated bed. Each reactor advantageously includes 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 withdrawn at the upper part of the reactor and reinjected at the lower part of the reactor.

[0162] The ebullated bed reactor preferably includes at least one inlet orifice located at or near the lower part of the reactor through which the feedstock is introduced together with the hydrogen, and in particular two inlet orifices in the case where the pyrolysis oil fraction 102 of the feedstock is introduced separately from the heavy hydrocarbon fraction 101, and an outlet orifice at or near the upper part of the reactor through which the first hydroconverted effluent 105 is withdrawn. The reactor also preferably comprises an inlet

and an outlet for the supported catalyst as already described previously in connection with the means for injection and withdrawal of the supported catalyst. The ebullated bed reactor also includes an expanded catalyst zone comprising the porous supported catalyst. The ebullated bed reactor also comprises a lower zone free of supported catalyst located below the expanded catalyst zone, and an upper zone free of supported catalyst located above the expanded catalyst zone. The feedstock in the ebullated bed reactor is continuously recirculated from the upper zone free of supported catalyst to the lower zone free of supported catalyst by means of a recycle pipe in communication with a boiling pump. Preferably, a funnel-shaped recycle pan is located at the upper part of the recycle pipe, through which pan the feedstock is sucked from the upper zone free of supported catalyst. The internal recycled feedstock is mixed with "fresh" feedstock and additional hydrogen gas.

[0163] The first supported hydroconversion catalyst used in the first hydroconversion step (b) may contain one or more elements from groups 4 to 12 of the Periodic Table of the Elements, which may or may not be deposited on a support. Use may advantageously be made of a catalyst comprising an amorphous support, such as silica, alumina, silica-alumina, titanium dioxide or combinations of these structures, and very preferably alumina.

[0164] The first supported catalyst may contain at least one non-noble group VIII metal chosen from nickel and cobalt, preferably nickel, said group VIII element preferably being used in combination with at least one group VIB metal chosen from molybdenum and tungsten; preferably, the group VIB metal is molybdenum.

[0165] In the present description, the groups of chemical elements are 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.

[0166] Advantageously, the first supported hydroconversion catalyst used in the first hydroconversion step (b) comprises an alumina support and at least one group VIII metal chosen from nickel and cobalt, preferably nickel, and at least one group VIB metal chosen from molybdenum and tungsten, preferably molybdenum. Preferably, the first supported hydroconversion catalyst comprises nickel as group VIII element and molybdenum as group VIB element.

[0167] The content of non-noble group VIII metal, in particular of nickel, is advantageously between 0.5% and 10%, expressed as weight of metal oxide (in particular NiO), and preferably between 1% and 6% by weight, and the content of group VIB metal, in particular molybdenum, is advantageously between 1% and 30%, expressed as weight of oxide of the metal (in particular molybdenum trioxide MoO₃), and preferably between 4% and 20% by weight. The contents of metals are expressed as weight percentages of metal oxide relative to the weight of the catalyst.

[0168] This first supported catalyst is advantageously used in the form of extrudates or beads. The beads have, for example, a diameter of between 0.4 mm and 4.0 mm. The extrudates have, for example, a cylindrical shape with a diameter of between 0.5 mm and 4.0 mm and with a length of between 1 mm and 5 mm. The extrudates may also be objects with a different shape, such as trilobes, tetralobes, which are regular or irregular, or other multilobes. Porous

supported catalysts of other forms may also be used. The size of these various forms of porous supported catalysts can be characterized by means of the equivalent diameter. The equivalent diameter is defined as six times the ratio of the volume of the particle to 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 catalysts are well known to those skilled in the art.

[0169] According to one or more embodiments of the invention, the first hydroconversion section **20** includes one or more hybrid bed reactors (i.e. hybrid ebullated-entrained beds), simultaneously including at least one first supported hydroconversion catalyst which is maintained in the reactor and at least one entrained catalyst which enters the reactor with the feedstock and is entrained out of the reactor with the effluents. In this case, as already described above in connection with step (a), an entrained catalyst precursor has been introduced before the feedstock is injected into the first hydroconversion reactor, and a colloidal or molecular catalyst, also known as a dispersed, entrained or slurry catalyst, may have formed upstream or in situ in the hybrid bed hydroconversion reactor. These entrained catalysts are well known to those skilled in the art.

[0170] The hybrid bed reactor comprises a solid phase which includes a porous supported catalyst in the form of an expanded bed, a liquid hydrocarbon-based phase including the colloidal or molecular catalyst-containing feedstock dispersed therein, and a gaseous phase comprising hydrogen.

[0171] The hybrid bed reactor is an ebullated bed hydroconversion reactor as described above, but comprising, in addition to the porous supported catalyst in the form of an expanded bed maintained in the reactor, the molecular or colloidal catalyst entrained out of the reactor with the hydroconverted liquid effluent **105**.

[0172] According to one or more embodiments, the functioning of the hybrid bed hydroconversion reactor is based on that of the ebullated bed reactor already described, and additionally involves the colloidal or molecular catalyst being dispersed throughout the feedstock in the hybrid bed reactor, including both in the expanded catalyst zone and in the supported catalyst-free zones, and thus available to stimulate upgrading reactions in what constitute catalyst-free zones in conventional ebullated bed reactors.

[0173] The presence of colloidal or molecular catalyst in the hybrid bed reactor provides additional catalytic hydrogenation activity, both in the expanded catalyst zone, in the recycle pipe, and in the lower and upper supported catalyst-free zones. The capping of free radicals outside the porous supported catalyst minimizes the formation of sediments and coke precursors, which are often responsible for the deactivation of the supported catalyst. This may allow a reduction in the amount of porous supported catalyst that would otherwise be required to perform a desired hydroconversion reaction. This may also reduce the rate at which the porous supported catalyst needs to be withdrawn and replenished. The use of a colloidal or molecular catalyst in a hybrid bed reactor may also allow the hydroconversion to be performed at higher temperatures than in the case of an ebullated bed reactor (supported catalyst(s) alone, without entrained catalyst), while remaining within the temperature ranges given above for step (b).

[0174] In one of the embodiments of the process according to the invention, a different first hydroconversion supported

catalyst may be used in each reactor of the first hydroconversion section, the supported catalyst specific to each reactor being suitable for the feedstock sent to that reactor. In one of the embodiments of the process according to the invention, several types of first supported catalyst are used in each reactor.

[0175] As is known, and for example described in patent FR3033797, the first hydroconversion supported catalyst, when spent, may be partly replaced with fresh supported catalyst, and/or spent supported catalyst but of higher catalytic activity than the spent supported catalyst to be replaced, and/or regenerated supported catalyst, and/or rejuvenated supported catalyst (catalyst coming from a rejuvenation zone in which most of the deposited metals are removed, before sending the spent and rejuvenated catalyst to a regeneration zone in which the carbon and sulfur it contains are removed, thus increasing the activity of the catalyst), by removing the spent supported catalyst preferably at the bottom of the reactor, and by introducing the replacement supported catalyst either at the top or at the bottom of the reactor. This replacement of spent supported catalyst is preferably performed at regular time intervals, and preferably in bursts or virtually continuously. This withdrawal and replacement is performed using a withdrawal and injection device advantageously allowing continuous functioning of this hydroconversion step.

[0176] By means of this supported catalyst withdrawal/injection operating mode, it is thus not necessary to stop the unit to change the spent catalyst, nor to increase reaction temperatures along the cycle to compensate for deactivation. Furthermore, working under constant operating conditions makes it possible to obtain constant product yields and qualities along the cycle.

[0177] Also, due to the fact that the supported catalyst is kept stirring by a significant recycling of liquid, the pressure drop over the reactor remains low and constant, and the reaction exotherms are rapidly averaged over the catalytic bed, which is thus virtually isothermal and does not require, for example, the injection of cooling streams (quenches).

[0178] One of the essential aspects of the invention lies in the capacity of the ebullated bed or hybrid ebullated-entrained bed reactor to continue the conversion of the pyrolysis oil into lighter products by virtue of the combination of a high temperature and of the presence of a catalyst which enables the hydrogenation of the unsaturated molecules (olefins or aromatics). The pyrolysis oil co-treatment thus makes it possible to improve the yield of certain cuts which are obtained in the hydroconverted effluent, in particular the gasoline cut.

[0179] Another advantage of the invention, linked to the use of a hydroconversion reactor operating in an ebullated or hybrid ebullated-entrained bed for the co-treatment of pyrolysis oil, is the scavenging of impurities such as silicon or metals by means of the supported catalyst. This allows low-impurity products to be obtained, which can thus be more readily treated in downstream processes, for instance fixed-bed hydrotreating processes. The advantage of the ebullated or hybrid ebullated-entrained bed is that the supported catalyst is continuously replaced, and it is easy to compensate for more severe deactivation by increasing catalytic replacement if necessary, notably in the case of pyrolysis oil heavily laden with impurities.

[0180] According to one or more embodiments, when step (b) is performed in one or more hybrid bed reactors, the

feedstock or the entrained catalyst precursor may be pre-mixed with an organic additive, before the feedstock is introduced into the first hydroconversion reactor of the first hydroconversion section **20**, so as notably to minimize fouling of the facilities prior to hydroconversion in the hybrid bed reactor(s). Without being bound by any theory, the organic additive, as a mixture with the feedstock, allows improved solubility of the catalyst precursor entrained in the feedstock, avoiding or reducing fouling in particular due to metal deposits in the facilities upstream of the hydroconversion reactor, such as in heating devices, and thus improving the dispersion of the entrained catalyst, thereby generating increased availability of metal active sites, promoting the hydrogenation of free radicals which are precursors of coke and sediments, and generating a substantial reduction in fouling of the facilities. Said organic additive, which is neither a catalyst nor a catalyst precursor (e.g. it contains no metal), has at least one carboxylic acid function and/or at least one ester function and/or at least one acid anhydride function. It preferably comprises at least 6, or even at least 8 carbon atoms, and more preferably at least 8 carbon atoms. According to one embodiment, it comprises 8 carbon atoms. For example, the organic additive may be 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, and mixtures thereof. The organic additive is preferably added during the mixing step so that the molar ratio of organic additive to active metal(s) of the catalyst precursor composition (e.g. Mo) is between 0.1:1 and 20:1, more preferably between 0.75:1 and 7:1, and even more preferably between 1:1 and 5:1.

(c) Optional Intermediate Separation Step

[0181] According to one or more preferred embodiments, the process according to the invention also comprises a separation step (c), which separates some or all of the first hydroconverted effluent **105**, to produce at least two cuts, one of which is a heavy cut boiling predominantly at a temperature greater than or equal to 350° C.

[0182] The other cut(s) are one or more light and intermediate cuts. The light cut thus separated contains mainly gases (H₂, HCl, H₂S, NH₃ and C₁-C₄), naphtha (or gasoline, cut boiling at a temperature below 150° C.), kerosene (or gas oil, cut boiling between 150° C. and 250° C.), and at least some of the diesel (fraction boiling between 250° C. and 375° C.). The light cut may then be sent at least in part to a fractionation unit (not represented in the figures) where the light gases are extracted from said light cut, for example by passing through an expansion vessel. This fractionation unit may be that of the fractionation step (e), notably in the case where a second hydroconversion step (d) is performed. The hydrogen gas thus recovered, which may have been sent to a purification and compression facility, may advantageously be recycled into the first hydroconversion step (b), and/or the second hydroconversion step (d) if performed. The hydrogen gas recovered can also be used in other installations of the refinery.

[0183] The optional separation step (c) is performed in a separation section (not shown in the figures), which comprises any separation means known to those skilled in the

art. Said separation section can comprise one or more expansion vessels arranged in series, and/or one or more steam stripping and/or hydrogen stripping columns, and/or an atmospheric distillation column, and/or a vacuum distillation column, and is preferably constituted of a single expansion vessel, commonly known as a "hot separator". The separation section may also comprise means for scrubbing the light cut mainly containing gases, by contact with an aqueous solution.

[0184] According to a preferred embodiment, the optional separation step (c) includes a hot separator operated at a temperature greater than or equal to 300° C., or even 350° C., so as to avoid the formation of ammonium chloride salts in the liquid phase; the gas phase of the hot separator, or at least one of the phases resulting from the subsequent separation of the gas phase from the hot separator, is advantageously placed in contact with water or a basic aqueous solution (sodium hydroxide solution, amine solution(s), for example) in order to at least partly remove the hydrogen chloride (HCl) and/or at least partly dissolve the ammonium chloride salts. The items of separation equipment or the separation vessels may comprise, at the bottom, a zone for the separate settling of a hydrocarbon fraction and of an aqueous fraction including chloride salts, or else may comprise a column for scrubbing the gases by bringing into contact with water or a basic aqueous solution.

(d) Optional Second Hydroconversion Step

[0185] According to one or more preferred embodiments (not shown in the figures), the process also comprises a second hydroconversion step, in at least one second ebullated bed or hybrid bed reactor comprising a second porous supported catalyst, in the presence of hydrogen, of some or all of the first effluent **105** resulting from step (b), or optionally of the heavy cut from step (c). This second hydroconversion step is performed so as to produce a second hydroconverted effluent. Said second hydroconverted effluent advantageously contains a larger amount of conversion products than the first hydroconverted effluent **105**, and notably an even lower content of hydrocarbons with a boiling point of at least 300° C., or of at least 350° C., 375° C., 450° C., 500° C., or 540° C. depending on the nature of the feedstock. The second hydroconverted effluent may have a further reduced Conradson carbon residue relative to the first hydroconverted effluent **105**, and optionally a further reduced amount of sulfur, and/or nitrogen, and/or metals, and/or silicon, and/or halogenated compounds (e.g. chlorine) and/or asphaltenes.

[0186] In particular, said second hydroconverted effluent may advantageously have a reduced content, relative to the first hydroconverted effluent **105** and/or relative to the feedstock, of sulfur, metals, silicon, halogenated compounds (e.g. chlorine), nitrogen, Conradson carbon, and asphaltenes.

[0187] The silicon and/or halogenated compounds (e.g. chlorine) content of the second hydroconverted effluent obtained on conclusion of step d) is advantageously reduced relative to the content of the same impurities (i.e. silicon and/or halogenated compounds such as chlorine) included in the first hydroconverted effluent **105** and/or in the feedstock.

[0188] Preferably, the second hydroconverted effluent includes a liquid fraction (PI+ fraction) having:

[0189] a silicon content of less than or equal to 5 ppm by weight, preferably less than or equal to 2 ppm by

weight, or even less than or equal to 1 ppm by weight relative to the total weight of said liquid part of the second hydroconverted effluent, and/or

[0190] a content of chlorine element of less than or equal to 10 ppm by weight, preferably less than or equal to 5 ppm by weight, or even less than or equal to 2 ppm by weight or even 1 ppm by weight, relative to the total weight of said liquid part of the second hydroconverted effluent.

[0191] The second hydroconversion step is performed in a similar manner to that described for the first hydroconversion step (b), and is not repeated here. This applies notably to the operating conditions, the equipment used and the porous supported hydroconversion catalysts used, with the exception of the details mentioned below.

[0192] As with the first hydroconversion step (b), the second hydroconversion step is performed in at least a second ebullated or hybrid bed reactor. It is preferably performed in one or more ebullated bed reactors if the first hydroconversion step is also performed in one or more ebullated bed reactors, and it is preferably performed in one or more hybrid bed reactors if the first hydroconversion step is performed in one or more hybrid bed reactors.

[0193] In this second hydroconversion step, the operating conditions may be similar to or different than those in hydroconversion step (d), with the temperature remaining in the range between 405° C. and 550° C., preferably between 405° C. and 500° C., more preferably between 405° C. and 450° C., and the amount of hydrogen introduced into the reactor remains in the range between 50 Nm³/m³ and 5000 Nm³/m³ of liquid feedstock, preferably between 100 Nm³/m³ and 3000 Nm³/m³, and even more preferably between 200 Nm³/m³ and 2000 Nm³/m³. The other pressure and HSV parameters are in identical ranges to those described for the hydroconversion step (d).

[0194] The operating temperature in the second hydroconversion step (d) may be higher than the operating temperature in the first hydroconversion step (b). This may allow more complete conversion of the as yet unconverted feedstock. Hydroconversion of liquid products from the first hydroconversion step and feedstock conversion are enhanced, as are the hydrotreating reactions such as hydrodesulfurization and hydrodenitrogenation, inter alia. The operating conditions are chosen to minimize the formation of solids (e.g. coke).

[0195] The second porous supported hydroconversion catalyst used in the second hydroconversion reactor may be the same as that used in the first hydroconversion reactor(s) of the first hydroconversion section 20, or may be another porous supported catalyst also suitable for hydroconversion of the treated feedstock, as defined for the first supported catalyst used in the first hydroconversion step (b).

[0196] As described in step (a), the pyrolysis oil fraction 102 of the feedstock is introduced, mixed or not with the heavy hydrocarbon fraction 101, into the first hydroconversion reactor of the first hydroconversion section 20. However, the pyrolysis oil fraction 102 may be placed in a hydroconversion reactor of the second hydroconversion section 20 without departing from the context of the present invention.

(e) Fractionation Step

[0197] The first hydroconverted effluent 105 from the hydroconversion step (b), or from the second hydroconver-

sion step (d) if such a step is performed, then undergoes at least in part a fractionation step (e) in a fractionation section 30.

[0198] This fractionation step (e) separates some or all of said hydroconverted effluent into several fractions, including at least one heavy liquid product 106b boiling predominantly at a temperature above 350° C., preferably above 500° C. and more preferably above 540° C. The heavy liquid product 106b contains a part boiling at a temperature above 540° C., called the residual fraction (or vacuum residue), which is the unconverted part. The heavy liquid product 106b may contain a portion of the gas oil fraction boiling between 250° C. and 375° C. and a portion boiling between 375° C. and 540° C. (also known as vacuum distillate).

[0199] This fractionation step thus produces at least two products including the heavy liquid product 106b as described above, the other product(s) 106a being light and intermediate cut(s).

[0200] The fractionation section 30 comprises any separation means known to those skilled in the art.

[0201] The fractionation section 30 may thus comprise one or more of the following items of separation equipment: one or more flash vessels arranged in series, preferably a sequence of at least two successive flash vessels, one or more steam and/or hydrogen stripping columns, an atmospheric distillation column, a vacuum distillation column.

[0202] According to one or more embodiments, this fractionation step (e) is performed by a sequence of at least two successive flash vessels.

[0203] According to one or more other embodiments, this fractionation step (e) is performed by one or more steam and/or hydrogen stripping columns.

[0204] According to one or more preferred embodiments, this fractionation step (e) is performed by an atmospheric distillation column, and more preferentially by an atmospheric distillation column and a vacuum column receiving the atmospheric residue.

[0205] According to the most preferred embodiment(s), this fractionation step (e) is performed by one or more flash vessels, an atmospheric distillation column and a vacuum column receiving the atmospheric residue. This configuration allows the size of any downstream deasphalter to be reduced, thus minimizing investment and operating costs.

[0206] The fractionation section 30 may also receive, in addition to some or all of the hydroconverted liquid effluent, one or more additional effluents, such as one or more hydrocarbon feedstocks external to the process (e.g. atmospheric and/or vacuum distillates, atmospheric and/or vacuum residues), part of the heavy cut from the separation step (c) if performed, part of one or more of the intermediate cuts from the fractionation step (e), part of a DAO or a light or heavy fraction of a DAO if a deasphalting step (f1) is performed. The fractionation section 30 may also comprise means for scrubbing one or more separated products by contact with an aqueous solution.

[0207] According to a preferred embodiment, the fractionation step (e) includes a hot separator operated at a temperature greater than or equal to 300° C., or even 350° C., so as to avoid the formation of ammonium chloride salts in the liquid phase; the gas phase of the hot separator, or at least one of the phases resulting from the subsequent separation of the gas phase of the hot separator, and also at least part of the liquid phase of the hot separator or at least one of the phases resulting from the subsequent separation of the liquid

phase of the hot separator, are advantageously placed in contact with water or a basic aqueous solution (sodium hydroxide solution, amine solution, for example) in order to at least partly remove the hydrogen chloride (HCl) and/or at least partly dissolve the ammonium chloride salts. The items of separation equipment or the separation vessels may comprise, at the bottom, a zone for the separate settling of a hydrocarbon fraction and of an aqueous fraction including chloride salts, or else may comprise a column for scrubbing the gases by bringing into contact with water or a basic aqueous solution.

[0208] According to a very preferred embodiment, when separation step c) is performed, at least part of the separation equipment is shared between steps c) and e).

(f) Subsequent Treatment Step(s)

[0209] One or more subsequent steps (f) of treatment of the heavy liquid product **106b** and/or of the other product(s) resulting from the fractionation step (e) may be performed.

[0210] Such a step (f) may comprise at least one step chosen from the list consisting of hydrotreating, steam cracking, fluidized bed catalytic cracking, hydrocracking, deasphalting and the extraction of lubricating oils. These examples of subsequent treatment are not exhaustive.

[0211] Specifically, the various hydrocarbon products that may result from fractionation step (e) in fractionation means **30** may be sent to various processes in the refinery, illustrated in the figures under the general reference **40**, and the details of all these post-treatments are not described here as they are generally known to those skilled in the art. For example, gas fractions, naphtha (gasoline), middle distillates, VGO, DAO may be sent to hydrotreating, steam cracking, fluidized bed catalytic cracking (FCC), hydrocracking, lubricant oil extraction, etc. processes. Residues (atmospheric or vacuum residues) may also be post-treated, or used for other applications such as gasification, production of bitumen, heavy fuel oils, etc. Heavy fractions, including residues, can also be recycled into the hydroconversion process, for example into a hydroconversion reactor in step (b) or (d).

[0212] According to one or more embodiments, the hydroconversion process includes a step (f1) of deasphalting, in a deasphalter, part or all of said heavy liquid product **106b** obtained in fractionation step (e), with at least one hydrocarbon-based solvent, to produce a deasphalted oil DAO and a residual asphalt ("SDA" Solvent DeAsphalting step).

[0213] Such a deasphalting step (f1) is performed under conditions well known to those skilled in the art. Reference may thus be made to the article by Billon et al. published in 1994 in Volume 49, No. 5 of the Revue de l'Institut Français du Pétrole, pages 495 to 507, to the book "Raffinage et conversion des produits lourds du pétrole" by J. F. Le Page, S. G. Chatila and M. Davidson, Edition Technip, pages 17-32 or to patents U.S. Pat. Nos. 4,239,616, 4,354,922, 4,354,928, 4,440,633, 4,536,283, and 4,715,946.

[0214] Deasphalting may be performed in one or more mixer-settlers or in one or more extraction columns. The deasphalter thus comprises at least one mixer-settler or at least one extraction column. Deasphalting is a liquid-liquid extraction generally performed at an average temperature of between 60° C. and 250° C. with at least one low-boiling hydrocarbon-based solvent, preferably a paraffinic solvent, preferably heavier than propane, preferentially containing from 3 to 7 carbon atoms. Preferred solvents include pro-

pane, butane, isobutane, pentane, isopentane, neopentane, hexane, isohexanes, C₆ hydrocarbons, heptane, C₇ hydrocarbons, more or less apolar light gasolines, and also mixtures obtained from the abovementioned solvents. Preferably, the solvent is butane, pentane or hexane, and also mixtures thereof. The solvent/feedstock (volume/volume) ratios entering the deasphalter are in general between 3/1 and 16/1, and preferably between 4/1 and 8/1. Preferably, the deasphalter comprises at least one extraction column, and preferably only one (e.g. as employed in the Solvahl™ process) in which the solvent/feedstock (volume/volume) ratios entering the deasphalter are preferably low, typically between 4/1 and 8/1, or even between 4/1 and 6/1. The deasphalter produces a DAO practically free of C₇ asphaltenes, said C₇ asphaltene content preferably being less than 2% by weight, more preferentially less than 0.5% by weight, even more preferentially less than 0.05% by weight, and a residual asphalt concentrating the majority of the impurities in the residue, said residual asphalt being drawn off. The DAO yield is generally between 40% and 95% by weight, depending on the operating conditions and solvent used, and on the feedstock sent to the deasphalter, notably the quality of the heavy liquid product **106b**.

[0215] According to one or more embodiments, the hydroconversion process includes at least one step (f2) of hydrotreatment, preferably in a fixed bed, performed in a hydrotreatment section, of one or more liquid products from the fractionation step (e). The hydrotreatment section may comprise at least one fixed-bed reactor containing n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment reaction section being fed with at least a portion of a liquid product obtained from step e) and a gas stream comprising hydrogen, to obtain a hydrotreated effluent.

[0216] Such a step involves hydrotreatment reactions that are well known to those skilled in the art, and more particularly hydrotreatment reactions such as the hydrogenation of aromatics or olefins, hydrodesulfurization and hydrodenitrogenation.

[0217] Said hydrotreatment reaction section is advantageously operated at an average temperature (Weight Average Bed Temperature (WABT) of between 250° C. and 430° C., preferably between 30° and 400° C., at a partial pressure of hydrogen of between 1.0 MPa abs. and 20.0 MPa abs., preferably between 3.0 MPa abs. and 15.0 MPa abs., and at an hourly space velocity (HSV) per volume of catalyst(s) of between 0.1 h⁻¹ and 10.0 h⁻¹, preferably between 0.1 h⁻¹ and 5.0 h⁻¹, preferentially between 0.2 h⁻¹ and 2.0 h⁻¹, preferably between 0.2 h⁻¹ and 1.0 h⁻¹. The hydrogen coverage in step f2) is advantageously between 50 Nm³ and 2000 Nm³, preferably between 100 Nm³ and 1000 Nm³, more preferentially between 120 Nm³ and 800 Nm³, of hydrogen per m³ of feedstock that feeds step f2).

[0218] The hydrotreatment section may comprise several, preferably two, reactors, which can operate in series and/or in parallel and/or in the PRS (lead and lag) and/or swing modes well known to those skilled in the art. Alternatively, the hydrotreatment section may comprise a single fixed-bed reactor containing n catalytic beds, n preferably being between 1 and 10, or even between 2 and 5.

[0219] Means for recovering catalyst fines and/or catalysts from hydroconversion may be used upstream or at the inlet to the hydrotreatment section, such as one or more filters or

even reactor internals, for example of the filter tray type, one example of which is described in patent FR3051375. The fixed-bed hydrotreatment catalyst used in step f2) may be chosen from known hydrotreatment and hydrodemetallization catalysts used notably for processing petroleum cuts. Known hydrotreatment catalysts are, for example, those described in the patents EP0113297, EP0113284, U.S. Pat. Nos. 6,589,908, 4,818,743 or 6,332,976. Known hydrodemetallization catalysts are, for example, those described in the patents EP0113297, EP0113284, U.S. Pat. Nos. 5,221,656, 5,827,421, 7,119,045, 5,622,616 and 5,089,463.

[0220] In particular, said hydrotreatment catalyst comprises a support, preferably a mineral support, and at least one metal element having a hydrodehydrogenating function.

[0221] Said metal element having a hydrodehydrogenating function advantageously comprises at least one group VIII element, preferably chosen from the group consisting of nickel and cobalt, and/or at least one group VIB element, preferably chosen from the group consisting of molybdenum and tungsten. The total content of oxides of metal elements from groups VIB and VIII is preferably between 0.1% and 40% by weight and more preferentially from 5% to 35% by weight relative to the total weight of the hydrotreatment catalyst. The weight ratio, expressed as metal oxide, between the group VIB metal(s) relative to the group VIII metal(s) is preferably between 1 and 20 and more preferentially between 2 and 10. For example, the hydrotreatment section of step f2) comprises a hydrotreatment catalyst including between 0.5% and 10% by weight of nickel, preferably between 1% and 8% by weight of nickel (expressed as nickel oxide NiO relative to the total weight of the hydrotreatment catalyst), and between 1.0% and 30% by total weight of molybdenum and/or tungsten, preferably between 3% and 29% by weight (expressed as molybdenum oxide MoO₃ or tungsten oxide WO₃ relative to the total weight of the hydrotreatment catalyst), on a mineral support.

[0222] The support for the hydrotreatment catalyst is advantageously chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof. The support may also contain dopant compounds (e.g. oxides chosen from boron oxide, in particular boron trioxide, zirconia, ceria, titanium oxide, phosphorus pentoxide and a mixture of these oxides).

[0223] Preferably, the hydrotreatment catalyst comprises an alumina support, preferably an alumina support doped with phosphorus and optionally boron. The alumina used may be, for example, a γ (gamma) or η (eta) alumina.

[0224] The hydrotreatment catalyst is advantageously used in the form of extrudates or beads, generally millimetric in size, for example with an equivalent diameter of between 0.4 mm and 4.4 mm.

[0225] Advantageously, the hydrotreatment catalyst used in step f2) has a specific surface area (measured by the BET method of determination by nitrogen adsorption according to the standard ASTM D3663) of greater than or equal to 250 m²/g, or even 300 m²/g, and advantageously less than or equal to 800 m²/g, or even 600 m²/g, or even 400 m²/g.

[0226] When it is desired to recycle part of the heavy residue fraction (e.g. part of the heavy liquid product **106b** and/or part of the residual asphalt, or part of the DAO) into the hydroconversion system (e.g. into the first hydroconversion reactor or upstream), it may be advantageous, in the case of hybrid bed reactor functioning, to leave the entrained

catalyst in the residues, and/or the residual asphalt fraction. A purge on the recycled stream may be performed, in general to prevent certain compounds from accumulating to excessive levels. It is specified that, for the purposes of the present invention, such a recycle stream does not form part of the feedstock as defined above, which includes the pyrolysis oil fraction **102** and the heavy hydrocarbon fraction **101**.

Analytical Methods Used

[0227] The analytical methods and/or standards used to determine the characteristics of the various streams, in particular the feedstock to be treated and effluents produced, are known to those skilled in the art. They are in particular listed below for information purposes. Other methods reputed to be equivalent can also be used, notably equivalent IP, EN or ISO methods.

TABLE 1

Description	Methods
Density at 15° C.	ASTM D4052
Sulfur Content	ISO 20846
Nitrogen Content	ASTM D4629
Bromine Number (Content of Olefins)	ASTM D1159
Content of Diolefins from the Maleic Anhydride Value	MAV Method ⁽¹⁾
Content of Oxygen-Containing Molecules	Infrared
Content of Paraffins	UOP990-11
Content of Naphthenes and Olefins	UOP990-11
Content of Aromatics	UOP990-11
Content of Halogens	ASTM D7359
Content of Chloride	ASTM D7536
Content of Metals:	ASTM D5185
P	
Fe	
Si	
Na	
Content of C ₇ Asphaltenes	ASTM D6560
Conradson Carbon	ASTM D482
Viscosity	ASTM D3236

⁽¹⁾ MAV method described in the article: C. López-García et al., Near Infrared Monitoring of Low Conjugated Diolefins Content in Hydrotreated FCC Gasoline Streams, Oil & Gas Science and Technology - Rev. IFP, Vol. 62 (2007), No. 1, pages. 57-68

EXAMPLES

[0228] The examples below are directed toward showing certain performance qualities of the process according to the invention.

[0229] These examples illustrate the possibility of co-treating a plastic pyrolysis oil in an H-Oil®-type ebullated bed hydroconversion process that converts it into lighter hydrocarbons, which can be used as bases for producing fuels, lubricants or any other product resulting from the refining of petroleum. The ability of the supported catalyst present in the H-Oil® process to scavenge the impurities present in the pyrolysis oil, thus facilitating the post-treatment of these products, is also demonstrated.

[0230] These examples were performed in a closed reactor (known as a batch reactor) representative of the operating conditions of the H-Oil® process.

[0231] Example 1 is a comparative example illustrating the performance qualities of the hydroconversion process for a reference feedstock (vacuum residue) without plastic pyrolysis oil.

[0232] Example 2 illustrates the performance qualities of an H-Oil® process with a feedstock including a plastic pyrolysis oil fraction and a fraction of the

reference feedstock (vacuum residue) used in Example 1. The mixture was employed during a pre-step of homogenization of the medium (optional step).

Feedstock:

[0233] The heavy fraction (I) of the feedstock is a “straight-run” vacuum residue (SR-VR) derived directly from the distillation of a petroleum crude. The fraction of plastic pyrolysis oil (II) of the feedstock is a pyrolysis oil resulting from a mixture of plastics and containing a high level of impurities.

[0234] The main characteristics of these two fractions of the feedstock are shown in Table 2 below.

100° C. to the reaction temperature and, in parallel, stirring is gradually increased from 500 to 1000 rpm. When the reaction temperature is reached, the pressure in the reactor is instantly adjusted to the target value by adding H₂. At this point, the reaction time is counted down. At the end of the experiment time, the reactor is rapidly cooled to stop the reaction, stirring is stopped when the reactor is at room temperature, and the liquid effluent and gases are collected for analysis.

Procedure of Example 2

[0237] The batch reactor is first charged with the same mass of catalyst of NiMo on alumina as for example 1 and

TABLE 2

Feedstock for the hydroconversion		Fraction I	Fraction II
Feedstock	—	SR-VR	Plastic pyrolysis oil
Density	—	1.004	0.834
Bromine Number	g/100 g	—	59
MAV	mg/g	—	36
Viscosity	cSt	922 (100° C.)	2.5 (40° C.)
Conradson Carbon	% by weight	18.1	—
C ₇ Asphaltenes	% by weight	6.1	—
Nickel + Vanadium	ppm by weight	257	<DL*
Si	ppm by weight	<DL*	92
Chlorine	ppm by weight	24	88
Nitrogen	ppm by weight	4895	2109
Sulfur	—	3.25% by weight	135 ppm by weight
Oxygen	% by weight	0.46	0.58
Hydrogen	% by weight	10.8	11.6
Content of 180° C.–	% by weight	0	51.0
Content of 180-350° C.	% by weight	0	34.0
Content of 350-540° C.	% by weight	13.9	12.1
Content of 540° C.+	% by weight	86.1	2.9

*DL: Detection Limit

[0235] The operating conditions of these examples are summarized in Table 3 below.

with the 90% by weight of SR-VR (fraction I of the feedstock), previously heated to 100° C. to make it less

TABLE 3

Example		1 Reference 100% Fraction I	2 10% Plastic pyrolysis oil
Feedstock		Fraction I (100% by weight) NC**	Fraction I (90% by weight) + Fraction II (10% by weight) 1
Duration of the homogenization steady stage	h	NC**	200
Temperature of the homogenization steady stage	° C.	NC**	200
Reaction temperature	° C.	420	420
Reaction time	min	150	150
Reaction pressure	MPa	16	16

**NC: Not concerned

Procedure of Example 1

[0236] The batch reactor is charged with a predefined mass of catalyst of NiMo on alumina and with the 100% of SR-VR (fraction I of the feedstock), previously heated to 100° C. to make it less viscous. The reactor is closed, purged with nitrogen, purged with hydrogen, and then pressurized with hydrogen up to a pressure of about 3 MPa. The reactor is then heated to 100° C. At this temperature, stirring is started at 500 rpm. Gradually, the temperature is raised from

viscous, then the 10% of plastic pyrolysis oil (fraction II of the feedstock) are added. The reactor is closed, purged with nitrogen, purged with hydrogen, and then pressurized with hydrogen up to a pressure of about 3 MPa. The reactor is then heated to 100° C. At this temperature, stirring is started at 500 rpm. Gradually, the temperature is raised from 100° C. to 200° C. and, in parallel, stirring is gradually increased from 500 to 1000 rpm. At 200° C., the pressure in the reactor is then 4 MPa. A one-hour steady stage at this temperature

is applied, although this step is optional, to ensure the good dispersion of the pyrolysis oil (fraction II of the feedstock) in the SR-VR (feedstock I). Following this steady stage, the batch reactor is heated to the reaction temperature, at which point the pressure in the reactor is instantly adjusted to the target value by adding H₂. At this point, the reaction time is counted down. At the end of the experiment time, the reactor is rapidly cooled to stop the reaction, stirring is stopped when the reactor is at room temperature, and the liquid effluent and gases are collected for analysis.

Overall Results and Performance Qualities:

[0238] The results relating to the total liquid effluent quality and hydroconversion performance qualities of these examples are detailed in Tables 4, 5 and 6 below.

TABLE 6-continued

Yields	Delta examples: 1-2
C ₃	0.0
C ₄	0.0
C ₁ -C ₄	0.2
PI-180° C.	3.8
180-350° C.	0.1
350-540° C.	-1.6
540° C.+	-2.1

[0239] The conversion of the 540° C.+ cut is calculated by the difference in mass between the feedstock and the total liquid effluent, as follows:

TABLE 4

Experiment		Example 1 (Reference 100% SR-VR feedstock)	Example 2 (with 10% of plastic pyrolysis oil)
Density	—	0.8989	0.8782
Conradson Carbon	% by weight	4.1	3.2
C ₇ Asphaltenes	% by weight	0.45	0.43
Sediments (IP-375)	% by weight	<DL*	0.04
V	ppm	<2	2.8
Si	ppm	<DL*	<DL*
Chlorine	ppm	<DL*	<DL*
Nitrogen	ppm	2915	2732
Sulfur	% by weight	0.5	0.39
Oxygen	% by weight	0.22	0.27
Hydrogen	% by weight	12.25	12.55

*DL: Detection Limit

**NC: Not concerned

TABLE 5

Experiment		Example 1 (Reference 100% SR-VR feedstock)	Example 2 (with 10% of plastic pyrolysis oil)
Yields			
H ₂ S	% weight/ feedstock	2.9	2.6
H ₂ O		0.3	0.3
NH ₃		0.3	0.3
C ₁		0.9	1.0
C ₂		0.5	0.6
C ₃		0.4	0.4
C ₄		0.2	0.2
C ₁ -C ₄		1.9	2.1
PI-180° C.		8.2	12.0
180-350° C.		25.6	25.7
350-540° C.		40.1	38.5
540° C.+		22.2	20.1
Conversion of 540° C.+ cut % by weight/540° C.+ feedstock		74.1	74.5

TABLE 6

Yields		Delta examples: 1-2
H ₂ S	% weight/ feedstock	-0.3
H ₂ O		0.0
NH ₃		0.0
C ₁		0.1
C ₂		0.1

$$\text{Conversion } 540^{+}\text{° C. (\%)} = \left(1 - \frac{\text{mass } 540^{+}\text{° C. effluent}}{\text{mass } 540^{+}\text{° C. feedstock}}\right) \times 100 \quad \text{Math 1}$$

[0240] It is observed that the presence of plastic pyrolysis oil does not affect the 540° C.+ conversion and thus allows a significant increase in the yield of the PI-180° C. cut, while at the same time reducing the yields of the heavy cuts.

[0241] It is also shown that despite the presence of silicon in the plastic pyrolysis oil, the hydroconversion products no longer contain any, indicating that the silicon has been scavenged by the supported catalyst. Similarly, the chlorine has been totally converted. The products resulting from this step are thus low in impurities and may notably be fed into fixed-bed hydrotreatment processes.

[0242] Moreover, the co-treatment of plastic pyrolysis oil does not appear to significantly destabilize the unconverted product, since the sediment content is only 0.04% by weight, which is a very low and perfectly tolerable value at the end of the hydroconversion process. The hydrotreating performance (notably hydrodenitrogenation and hydrodesulfurization) is also maintained, or even improved.

1. A process for the hydroconversion of a feedstock comprising a plastic and/or solid recovered fuel pyrolysis oil fraction (102) and a fossil-based heavy hydrocarbon fraction (101) containing a portion of at least 50% by weight with a boiling point of at least 300° C. and containing sulfur and nitrogen, said pyrolysis oil fraction (102) constituting less than 50% by weight of said feedstock, said process comprising:

- (a) conditioning and introducing said feedstock into a first hydroconversion section (20) including at least a first ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor comprising a first porous supported hydroconversion catalyst;
- (b) a first step of hydroconverting said feedstock in the presence of hydrogen in said first hydroconversion section (20) to obtain a first hydroconverted effluent (105);
- (c) optionally, a step of separating part or all of said first effluent resulting from step (b), to form at least one heavy cut boiling predominantly at a temperature greater than or equal to 350° C.;
- (d) optionally, a second hydroconversion step in a second hydroconversion section including at least a second ebullated bed or hybrid ebullated-entrained bed hydroconversion reactor of part or all of said first effluent resulting from step (b) or optionally of said heavy cut resulting from step (c), said second hydroconversion reactor comprising a second porous supported catalyst and operating in the presence of hydrogen, to produce a second hydroconverted effluent;

step (b) and optional step (d) being performed at an absolute pressure of between 2 MPa and 38 MPa, at a temperature of between 300° C. and 550° C., at an hourly space velocity of between 0.05 h⁻¹ and 10 h⁻¹, and with an amount of hydrogen of between 50 Nm³/m³ and 5000 Nm³/m³; and

- (e) a step of fractionating all or some of said first hydroconverted effluent from step (b) or of said second hydroconverted effluent from step (d), in a fractionation section (30), to produce at least one heavy liquid product (106b) which boils predominantly at a temperature greater than or equal to 350° C., said heavy liquid product containing a residual fraction boiling at a temperature greater than or equal to 540° C.

2. The process as claimed in claim 1, wherein, in step (a), the pyrolysis oil fraction (102) and the heavy hydrocarbon fraction (101) of the feedstock are premixed before being introduced into said at least one first hydroconversion reactor of the first hydroconversion section (20).

3. The process as claimed in claim 1, wherein, in step (a), the pyrolysis oil fraction (102) of the feedstock is introduced separately from the heavy hydrocarbon fraction (101) into said at least one first hydroconversion reactor of the first hydroconversion section (20).

4. The process as claimed in claim 1, wherein step (a) includes a step of preheating said heavy hydrocarbon fraction (101), and optionally a step of preheating the pyrolysis oil fraction (102), before the feedstock is introduced into the first hydroconversion reactor of the first hydroconversion section (20).

5. The process as claimed in claim 1, wherein the pyrolysis oil fraction (102) constitutes between 1% and 45% by weight of said feedstock.

6. The process as claimed in claim 1, wherein the feedstock is constituted of said of pyrolysis oil fraction (102) and of said heavy hydrocarbon fraction (101), said pyrolysis oil fraction (102) constituting between 1% and 45% by weight of said feedstock and the heavy hydrocarbon fraction (101) constituting between 55% and 99% by weight, of the feedstock.

7. The process as claimed claim 1, wherein the pyrolysis oil fraction (102) is a plastic pyrolysis oil.

8. The process as claimed in claim 1, wherein the heavy hydrocarbon fraction (101) is chosen from the group consisting of a crude oil, a topped crude oil, an atmospheric residue or a vacuum residue resulting from the atmospheric and/or vacuum distillation of a crude oil or of an effluent originating from a thermal conversion, hydrotreating, hydrocracking or hydroconversion unit, an aromatic cut extracted from a unit for the production of lubricants, a deasphalted oil resulting from a deasphalting unit, an asphalt resulting from a deasphalting unit, a residual fraction resulting from direct coal liquefaction, a vacuum distillate resulting from direct coal liquefaction, and mixtures thereof.

9. The process as claimed in claim 8, wherein the heavy hydrocarbon fraction (101) is a vacuum residue.

10. The process as claimed in claim 1, wherein said process includes separation step (c) of separating part, or all, of the first hydroconverted effluent (105) obtained from step (b) to produce at least the heavy cut boiling predominantly at a temperature greater than or equal to 350° C., and includes the second step (d) of hydroconverting said heavy cut.

11. The process as claimed in claim 1, wherein the hydroconversion reactor(s) of the first hydroconversion section (20) in step (b), and optionally in hydroconversion step (d), are hybrid ebullated-entrained bed reactors, said process also including a step of introducing a catalyst precursor (104) into the feedstock prior to injection of said feedstock into said at least one first hybrid ebullated-entrained bed reactor of the first hydroconversion section (20), in such a way that a colloidal or molecular catalyst is formed when said feedstock reacts with sulfur.

12. The process as claimed in claim 1, wherein the first hydroconversion catalyst, and optionally the second hydroconversion catalyst, contains at least one non-noble group VIII metal chosen from nickel and cobalt, and at least one group VIB metal chosen from molybdenum and tungsten, and including an amorphous support.

13. The process as claimed in claim 1, wherein step (b) and the optional step (d) are performed at a temperature of between 405° C. and 450° C.

14. The process as claimed in claim **1**, wherein said process includes separation step (c) and separation step (c) is performed in a separation section, and in which said separation section and/or the fractionation section (**30**) in step (e) include means for washing at least one separated cut by contact with an aqueous solution.

15. The process as claimed in claim **1**, further comprising a step (f) of further processing the heavy liquid product (**106b**) and/or of the other product(s) from fractionation step (e), said step (f) comprising at least one step chosen from the list consisting of hydrotreating, steam cracking, fluidized bed catalytic cracking, hydrocracking, deasphalting, lubricant oil extraction, and preferably a fixed-bed hydrotreatment step (f2) in a hydrotreatment section, said hydrotreatment section preferably comprising at least one fixed-bed reactor containing n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment section being fed with at least a portion of a liquid product from step e) and a gaseous stream comprising hydrogen, to obtain a hydrotreated effluent.

16. A product obtained via the process as claimed in claim **1**.

17. The hydroconverted effluent as claimed in claim **16**, obtained on conclusion of the first hydroconversion step (b) or of the second hydroconversion step (d), and including a liquid part comprising, relative to the total weight of said liquid part of said effluent, a silicon content of less than or equal to 5 ppm by weight, and/or a chlorine element content of less than or equal to 10 ppm by weight.

18. The process as claimed in claim **1**, wherein step (a) includes a step of preheating said heavy hydrocarbon fraction (**101**) to a temperature of between 280° C. and 450° C., and optionally a step of preheating the pyrolysis oil fraction (**102**), before the feedstock is introduced into the first hydroconversion reactor of the first hydroconversion section (**20**).

19. The process as claimed in claim **1**, wherein the pyrolysis oil fraction (**102**) constitutes between 2% and 30% by weight of said feedstock.

20. The process as claimed in claim **1**, in which the feedstock is constituted of said of pyrolysis oil fraction (**102**) and of said heavy hydrocarbon fraction (**101**), said pyrolysis oil fraction (**102**) constituting between 2% and 30% by weight of said feedstock and the heavy hydrocarbon fraction (**101**) between 70% and 98% by weight of the feedstock.

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