

METHOD FOR TREATING PYROLYSIS OIL, INCLUDING A PREFRACTIONATION

TECHNICAL FIELD

5 The present invention is in the field of the recycling of plastics and/or tyres and/or solid recovered fuels (SRFs). More particularly, the present invention relates to a process for treating a feedstock comprising a plastic and/or tyre and/or SRF pyrolysis oil, including in particular a prefractionation of the feedstock making it possible to extract a naphtha cut, said naphtha cut subsequently being subjected to a treatment which makes it possible to remove
10 the impurities specifically contained in this cut for the purpose of using this cut in particular as a feedstock for a steam cracker for producing olefins.

PRIOR ART

Plastics obtained from collection and sorting channels or recycled tyres or else solid
15 recovered fuels (SRFs) may undergo a pyrolysis step in order to upgrade them. Pyrolysis consists in heating, with or without a catalyst, a feedstock containing plastic and/or recycled tyres and/or else SRFs in the absence of oxygen, leading to the formation of three main products: a hydrocarbon phase liquid at ambient temperature and also referred to as pyrolysis oil, a light gas phase also referred to as pyrolysis gas, and a solid residue also
20 referred to as char.

The liquid hydrocarbon phase, the pyrolysis oil, can be upgraded in a unit for the storage of petrol, kerosene or gas oil fuels.

Another route for upgrading pyrolysis oils is the use of these pyrolysis oils as feedstock of a steam cracking unit in order to (re)create olefins, the latter being constituent monomers of
25 certain polymers.

However, pyrolysis oils have impurities at contents that are often high and incompatible with direct storage in a fuel storage unit or with steam cracking units or units located downstream of steam cracking units, in particular polymerization processes and selective hydrogenation processes. These impurities can give rise to operability problems and in particular problems
30 of corrosion (in particular due to the presence of chlorine), of coking or of catalyst deactivation, or else incompatibility problems in the uses of the target polymers. The presence of diolefins can also result in problems of instability of the pyrolysis oil,

characterized by the formation of gums. The gums and the insoluble materials possibly present in the pyrolysis oil can give rise to problems of clogging in the processes.

One route for removing these impurities contained in plastic and/or tyre pyrolysis oils is to carry out hydrotreating (HDT) in the presence of catalysts. Such processes are, for example,
5 described in WO2018/055555, WO2021/165178 or else WO2022/144235. All these processes share the fact that the entirety of the pyrolysis oil is hydrotreated (without prefractionation).

However, the various impurities which are contained in the pyrolysis oil and which it is desired to remove are generally found in various fractions of this oil. This is because,
10 depending on the origin of the pyrolysis oil, the oil can have a fairly wide range of boiling points (for example between 40°C and 700°C). Some impurities, in particular chlorine, silicon or else diolefins and monoolefins, are usually found instead in the lighter fraction of the oil (naphtha cut), while other impurities, such as for example sulfur, nitrogen and metals, are concentrated more in the heavier fractions of the oil.

15 The present invention proposes to adapt the type of treatment for removing the impurities to the various fractions of the oil by carrying out a prefractionation beforehand. It aims in particular to produce a naphtha cut for the purpose of using this cut as a feedstock for a steam cracker to produce olefins.

During the steam cracking step, the yields of light olefins desired for the petrochemical
20 industry, in particular ethylene and propylene, are strongly dependent on the quality of the feedstocks sent to steam cracking. The BMCI (Bureau of Mines Correlation Index) is often used to characterize hydrocarbon cuts. Overall, the yields of light olefins increase when the paraffin content increases and/or when the BMCI decreases. Conversely, the yields of undesired heavy compounds and/or of coke increase when the BMCI increases.

25 Although a heavy cut of middle distillate type can be sent to a steam cracking unit, few refiners favour this option. This is because the heavy cut has a high BMCI and contains, with respect to the naphtha cut, more naphthenic, naphthenic-aromatic and aromatic compounds, thus leading to a higher C/H ratio. This high ratio is a cause of coking in the steam cracker, thus requiring steam cracking furnaces dedicated to this cut. Furthermore, the steam
30 cracking of such a heavy cut produces a smaller amount of products of interest which are notably ethylene and propylene, but more pyrolysis gasoline.

It would thus be advantageous to extract the naphtha cut from the pyrolysis oil and to remove the specific impurities which it contains by a treatment dedicated to this cut for the purpose of using this cut as a feedstock for a steam cracker.

5 Pyrolysis oil treatment processes with prefractionation of the pyrolysis oil are, for example, described in WO2018/069794, EP4108737, WO2022/034287 and US2022/340824 without, however, adapting the treatment of a fraction to the nature of the impurities, as proposed in the present invention.

10 Document US2023/0013013 describes a process for treating plastics including a pyrolysis step for obtaining a pyrolysis oil which is subsequently fractionated to give a fraction comprising naphtha and diesel and a vacuum gas oil (VGO) fraction. The fraction comprising naphtha and diesel is subsequently subjected to three consecutive hydrotreating steps: a first for removing diolefins, a second for removing monoolefins and a third for removing sulfur and nitrogen. This document also describes the possibility of a prefractionation to give 3 fractions, a naphtha fraction, a diesel fraction and a vacuum gas oil fraction. The naphtha fraction and
15 the diesel fraction are subsequently independently subjected, in parallel, to the three hydrotreating steps described above. The vacuum gas oil fraction, for its part, can be subjected to a hydrodemetallization step or a solvent deasphalting step. This document is targeted at the production of fuels.

20 Document WO2022/144491 describes a process for treating a pyrolysis oil comprising a stripping step which makes it possible to separate the oil into a distillate cut comprising diolefins and naphtha and a heavier cut. The distillate cut is subsequently subjected to hydrotreating, which makes it possible to remove the diolefins, and then subjected to a distillation in order to recover at least one naphtha cut which is again hydrotreated in order to provide a naphtha cut which is suitable for a steam cracker. The other cuts can be mixed
25 with crude oil and later processed in an oil refinery.

The process according to the invention proposes to extract a naphtha cut by prefractionation, then to remove the impurities contained in this highly reactive cut by a selective hydrogenation treatment and then by a hydrogenation treatment, optionally followed by suitable hydrotreating.

30 The prefractionation makes it possible to extract a naphtha cut resulting from a pyrolysis oil and compatible in distillation interval with the operation of a steam cracking furnace but also to concentrate certain impurities harmful to the steam cracking unit (olefins, diolefins, chlorine compounds and silicon compounds) for the treatment thereof. Treatment by the

process according to the invention makes it possible to eliminate a large part of the impurities concentrated in the naphtha cut and to make it compatible with use in a steam cracker.

The process according to the invention makes it possible to achieve the purity targets indicated while controlling the high reaction exotherms generated by the concentration of monoolefins/diolefins within this lighter cut (naphtha cut), in particular by adapting the number of catalyst beds, and by injecting a liquid and/or gaseous diluent stream (hydrotreated naphtha cut, hydrogen-rich gas stream) if required. The naphtha cut is in particular subjected to a selective hydrogenation step making it possible to eliminate in particular the diolefins, then to a hydrogenation step making it possible to eliminate in particular the silicon and chlorine and the monoolefins. Depending on the content of the impurities contained in the hydrogenated naphtha cut, it can subsequently be subjected to a hydrotreating step enabling in particular the sulfur and nitrogen to be removed. The naphtha cut thus treated meets the specifications of a steam cracker feedstock.

The treatment of the light fraction of the pyrolysis oil (naphtha cut) and not of the oil in its entirety also makes it possible to moderate the operating conditions (hydrogen partial pressure, temperature, and the like). At an identical hourly space velocity compared to a unit for treating the whole of the pyrolysis oil, a saving is made with regard to the capacity of the unit, and also with regard to the investment cost and the footprint.

By virtue of the prefractionation, certain impurities which are particularly harmful to the steam cracking unit end up more concentrated in the light naphtha fraction. Conversely, these same compounds are less concentrated in the heavier cut(s), which favours the treatment thereof in downstream units. It(they) generally contain(s) little or no diolefins. In addition, it(they) contain(s) less in the way of chlorine compounds and silicon compounds than the naphtha cut. The heavy cut(s) can thus be subjected to subsequent specifically adapted treatments, of hydrotreating, then hydrocracking, or fluid catalytic cracking type, optionally in co-processing with feedstocks of fossil or biobased origin. The process according to the invention thus offers flexibility with regard to the use of the heaviest fractions of the pyrolysis oil.

Another advantage of the invention is that of preventing risks of plugging and/or of corrosion of the treatment unit in which the process of the invention is carried out, the risks being exacerbated by the presence, often in large amounts, of diolefins, of metals and of halogen compounds. These risks of plugging and/or of corrosion are in particular decreased by a separation step involving washing with an aqueous solution. This washing/separation step makes it possible in particular to remove ammonium chloride salts, which are formed by

reaction between chloride ions, released by hydrogenation of chlorine compounds in the form of HCl, in particular during the hydrogenation step, followed by dissolution in water, and ammonium ions, generated by the hydrogenation of nitrogen compounds in the form of NH_3 during the hydrogenation and/or hydrotreating step and/or supplied by injection of an amine when the content of chlorine compounds is high, followed by dissolution in water.

SUMMARY OF THE INVENTION

More specifically, the invention relates to a process for treating a feedstock comprising a plastic and/or tyre and/or solid recovered fuel pyrolysis oil, said process comprising the following steps:

- 10 a) a step of prefractionating the feedstock in order to obtain a naphtha cut and at least one heavier cut,
- b) a selective hydrogenation step carried out in a reaction section fed with said naphtha cut and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature of between 100°C and 260°C , a hydrogen
- 15 partial pressure of between 1.0 and 10.0 MPa abs. and an hourly space velocity of between 0.1 and 10.0 h^{-1} , in order to obtain a selectively hydrogenated effluent,
- c) a hydrogenation step carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrogenation catalyst, said hydrogenation reaction section
- 20 being fed at least with said selectively hydrogenated effluent obtained from step b) and a gas stream comprising hydrogen, said hydrogenation reaction section being employed at an average temperature between 180°C and 380°C , a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h^{-1} , in order to obtain a hydrogenated effluent,
- 25 d) optionally, a hydrotreating step carried out in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with said hydrogenated effluent obtained from step c) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an
- 30 average temperature between 200°C and 400°C , a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h^{-1} , in order to obtain a hydrotreated effluent;
- e) a separation step, fed with the hydrogenated effluent obtained from step c) or with the hydrotreated effluent obtained from step d) and an aqueous solution, said step being carried

out in a separation section at a temperature between 20°C and 300°C, in order to obtain at least a gaseous effluent, an aqueous effluent and a naphtha cut stripped of its impurities.

According to a variant, the process comprises the hydrotreating step d).

5 According to a variant, the naphtha cut obtained in step e) is at least partly sent to a steam cracking unit.

According to a variant, the steam cracking is carried out in at least one pyrolysis furnace at a temperature of between 700°C and 900°C and at a pressure of between 0.05 and 0.3 MPa relative in the presence of steam.

10 According to a variant, a liquid and/or gaseous diluent is injected in step b), c) and/or d).

According to a variant, the liquid diluent is a portion of the naphtha cut obtained in step e) and the gaseous diluent is the gaseous effluent obtained in step e).

15 According to a variant, the process comprises at least one step of pretreatment of the feedstock or of the naphtha cut obtained in step a), said pretreatment step being carried out before or after the prefractionation step a) and upstream of the selective hydrogenation step b) and comprises an adsorption step and/or a filtration step and/or a centrifugation step and/or a decantation step and/or an electrostatic separation step and/or a step of washing with an aqueous solution and/or a gas stripping step.

20 According to a variant, said selective hydrogenation catalyst of step b) comprises a support chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising at least one group VIII element and/or at least one group VIB element.

25 According to a variant, said hydrogenation catalyst of step c) comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising either at least one group VIII element and at least one group VIB element, or at least one group VIII element.

30 According to a variant, said hydrotreating catalyst of step d) comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising at least one group VIII element and/or at least one group VIB element.

According to a variant, the feedstock consists of a plastic and/or tyre and/or solid recovered fuel pyrolysis oil.

According to a variant, said prefractionation step a) is carried out so as to obtain said naphtha cut and at least one middle distillate cut and a vacuum gas oil cut.

- 5 According to a variant, at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut is reintroduced in step c) and/or d).

According to a variant, at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut is subjected to a dedicated hydrotreating step, in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst
10 beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with said heavy cut, or said middle distillate cut and/or said vacuum gas oil cut and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an average temperature between 250°C and 430°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and
15 an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrotreated heavy effluent.

According to a variant, at least one portion of the hydrotreated heavy effluent is sent to a hydrocracking step carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each
20 comprising at least one hydrocracking catalyst, said hydrocracking reaction section being fed at least with said hydrotreated heavy effluent and a gas stream comprising hydrogen, said hydrocracking reaction section being employed at an average temperature between 250°C and 480°C, a hydrogen partial pressure between 1.5 and 20.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrocracked effluent.

25 According to a variant, at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut, or of the hydrotreated heavy effluent is sent to a fluid catalytic cracking step carried out in a fluid catalytic cracking reaction section in a substantially vertical reactor, either in riser mode or in downer mode, in the presence of a zeolite catalyst at a reactor temperature of between 450°C and 600°C with a contact time in
30 the reactor of less than 1 minute.

The invention also relates to a product obtained by the process according to the invention.

According to one variant, the product comprises a content of biological carbon according to ASTM D6866 of between 0% and 70% by weight.

In the remainder of the text, the term "pyrolysis oil" is understood to mean an oil resulting from the pyrolysis of plastics and/or of tyres and/or of SRFs, unless otherwise indicated. When the provenance of the pyrolysis oil is important, its origin is added (for example *tyre pyrolysis oil*).

- 5 According to the present invention, the expressions "of between ... and ..." and "between ... and ..." are equivalent and mean that the limit values of the interval are included in the described range of values. Should such not be the case and should the limiting values not be included in the range described, such a clarification will be provided by the present invention.

- 10 In the present description, the term "comprise" is synonymous with (means the same thing as) "include" and "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".

- 15 For the purposes of the present invention, the various parameter ranges for a given step, such as the pressure ranges and the temperature ranges, can be used alone or in combination. For example, for the purposes of the present invention, a range of preferred pressure values can be combined with a range of preferred temperature values.

Hereinafter, particular and/or preferred embodiments of the invention may be described. They can be employed separately or combined together, without limitation of combination when this is technically feasible.

- 20 In the text hereinbelow, 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 (or VIIIB) according to the CAS classification corresponds to the metals of columns 8, 9 and 10 according to the new IUPAC classification.

- 25 The content of metals is measured by X-ray fluorescence.

DETAILED DESCRIPTION

The feedstock

According to the invention, the feedstock comprises a plastic and/or tyre and/or SRF pyrolysis oil.

- 30 Plastic waste is generally a mixture of several polymers. The feedstock used in the process according to the invention may comprise, alone or as a mixture, (low and/or high density) polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride and polystyrene.

Furthermore, depending on the applications, the plastics may contain, in addition to polymers, other compounds, such as plasticizers, pigments, dyes or else residues of polymerization catalysts. Plastic waste may additionally contain, in a minor amount, biomass originating, for example, from household waste.

- 5 With regard to tyres, these are mainly constituted of rubbers, for their elastic property (mixture of elastomers of the type of crosslinked synthetic and natural rubbers, with the addition of adjuvants of the type of silica, resin, sulfur, zinc oxide, carbon black, and the like), and of textile and metal fibres, for their reinforcing property.

- 10 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
15 (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.

- 20 The pyrolysis oil included in the feedstock, whether obtained from tyres, plastics and/or SRFs, results from a step of pyrolysis of a feedstock containing tyres, plastic(s) and/or SRFs in a pyrolysis unit.

The pyrolysis step can be carried out by a thermal or catalytic pyrolysis treatment or else be prepared by hydropyrolysis (pyrolysis in the presence of a catalyst and hydrogen).

The pyrolysis step is generally performed at a temperature of between 250°C and 750°C.

The pyrolysis step can be carried out under conditions that are more or less severe.

- 25 The low-severity pyrolysis step is carried out at a temperature between 250°C and 450°C, preferably between 275°C and 425°C and particularly preferably between 300°C and 400°C. The low-severity pyrolysis step produces pyrolysis oils rich in monoolefins and diolefins, and also a significant amount of aromatics, and which may include chlorine compounds.
- 30 The high-severity pyrolysis step is performed at a temperature between 450°C and 750°C, preferably between 500°C and 700°C, and particularly preferably between 550°C and 650°C. The high-severity pyrolysis step produces pyrolysis oils rich in aromatics, and which may include chlorine compounds.

The pyrolysis unit can comprise one or more reactors configured to convert the feedstock into gas-phase and liquid-phase products (for example simultaneously). The reactor(s) can contain one or more beds of inert materials or of pyrolysis catalysts comprising sand, zeolite or combinations thereof. Generally, the pyrolysis catalyst is capable of transferring heat to the components subjected to the pyrolysis process in the pyrolysis unit.

The pyrolysis unit can comprise one or more items of equipment, for example one or more heated extruders, a heated rotary kiln, heated tank-type reactors, empty heated containers, closed heated surfaces where the feedstock flows along the wall, containers surrounded by furnaces or furnaces or other items of equipment that provide a heated surface.

In one or more embodiments of the pyrolysis unit, a purge gas is used in all or part of the pyrolysis stages(s) to improve the cracking of the plastics, to produce products of value, to provide a feed for the steam cracking, or combinations thereof. The purge gas may comprise hydrogen (H₂), nitrogen (N₂), steam, product gases, or combinations thereof.

The pyrolysis oil, whether derived from tyres, plastics and/or SRFs, generally has a range of boiling points of between 40°C and 1000°C, preferably of between 45°C and 650°C, in a preferred way of between 45°C and 550°C.

The pyrolysis oil, whether derived from tyres, plastics and/or SRFs, generally has a density, measured at 15°C according to the ASTM D4052 method, of between 0.75 and 1.05 g/cm³, preferably of between 0.75 and 0.95 g/cm³.

The pyrolysis oil, advantageously in liquid form at ambient temperature, comprises in particular a mixture of hydrocarbon compounds, especially paraffins (n-paraffins and isoparaffins), olefins (monoolefins and/or diolefins), naphthenes and aromatics. In particular, depending on the origin of the feedstock treated by the pyrolysis unit, the pyrolysis oil can comprise up to 70% by weight of paraffins, up to 90% by weight of naphthenes, up to 90% by weight of olefins and up to 90% by weight of aromatics, it being understood that the sum of the paraffins, naphthenes, olefins and aromatics is equal to 100% by weight of the hydrocarbon compounds.

The pyrolysis oil can comprise diolefins. The content of diolefins is commonly determined indirectly as the maleic anhydride value (MAV). The method is based on the Diels-Alder addition reaction between the conjugated diolefins and the maleic anhydride. The method for the determination of the MAV is described in 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, pp. 57-68. The MAV is expressed

in mg of maleic anhydride having reacted with 1 g of sample (mg/g). The MAV varies between 5 and 100 mg/g in the pyrolysis oils.

The pyrolysis oil, whether derived from tyres, plastics and/or SRFs, can contain a portion of compounds of biological origin, such as, for example, a tyre pyrolysis oil which is produced from elastomers of natural rubber type, or a plastic and/or SRF pyrolysis oil produced from plastic waste and/or SRF which may contain, in a minor amount, biomass originating, for example, from household waste. The content of biological carbon (according to the C¹⁴ isotope radiocarbon analytical method according to ASTM D6866) may be between 0 and 70% by weight, preferably between 0.1% and 60% by weight, relative to the total weight of the pyrolysis oil. In the case of a tyre pyrolysis oil, the latter can comprise a content of biological carbon (according to the C¹⁴ isotope radiocarbon analytical method according to ASTM D6866) of between 20% and 70% by weight, preferably of between 30% and 60% by weight, relative to the total weight of the pyrolysis oil. This makes it possible to incorporate a biological composition into the products of the process according to the invention.

The pyrolysis oil additionally can comprise, and usually comprises, impurities, such as metals, in particular iron, silicon or halogen compounds, in particular chlorine compounds. These impurities can be present at high contents, for example up to 500 ppm by weight or else 700 ppm by weight, indeed even 1000 ppm by weight, and even 5000 ppm by weight, of halogen elements (in particular chlorine but also bromine, fluorine or iodine) contributed by halogen compounds, and generally between 1 and 1000 ppm by weight or between 1 and 700 ppm by weight or else between 1 and 500 ppm by weight of halogen elements. The pyrolysis oil can contain up to 500 ppm by weight or else 700 ppm by weight, indeed even 1000 ppm by weight and even 5000 ppm by weight of chlorine element contributed by chlorine compounds, and generally between 1 and 1000 ppm by weight or between 1 and 700 ppm by weight or else between 1 and 500 ppm by weight of chlorine element. The pyrolysis oil can contain up to 50 ppm by weight or else 100 ppm by weight of bromine element contributed by bromine compounds, and generally between 1 and 100 ppm by weight or between 1 and 50 ppm by weight of bromine element.

The oil can comprise up to 200 ppm by weight, indeed even 1500 ppm by weight, of metal or semi-metal elements, and generally between 1 and 200 ppm by weight or between 1 and 1500 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 metal nature, referred to as metals or metallic or semi-metallic elements. In particular, the metals or metallic or semi-metallic elements comprise silicon, iron or both of these elements. The pyrolysis oil can in particular comprise up to 200 ppm by weight or else

1000 ppm by weight of silicon, and generally between 1 and 200 ppm by weight or between 1 and 1000 ppm by weight or else between 1 and 500 ppm by weight of silicon. The pyrolysis oil can in particular comprise up to 50 ppm by weight or else 100 ppm by weight of iron, and generally between 1 and 50 ppm by weight or between 1 and 100 ppm by weight of iron. The
 5 pyrolysis oil can also comprise phosphorus, sodium, calcium, potassium and magnesium.

The pyrolysis oil can also comprise other impurities, such as heteroelements contributed in particular by sulfur compounds, oxygen compounds and/or nitrogen compounds, at contents generally of less than 40 000 ppm by weight of heteroelements and preferably of less than 15 500 ppm by weight of heteroelements, and generally between 1 and 40 000 ppm by
 10 weight or between 1 and 15 500 ppm by weight of heteroelements.

The sulfur compounds are generally present in a content of less than 15 000 ppm by weight and preferably of less than 10 000 ppm by weight, and generally between 1 and 15 000 ppm by weight or between 1 and 10 000 ppm by weight of sulfur compounds.

The oxygen compounds are generally present in a content of less than 15 000 ppm by
 15 weight and preferably of less than 10 000 ppm by weight, and generally between 1 and 15 000 ppm by weight or between 1 and 10 000 ppm by weight of oxygen compounds.

The nitrogen compounds are generally present in a content of less than 10 000 ppm by weight and preferably of less than 5000 ppm by weight, and generally between 1 and 10 000 ppm by weight or between 1 and 5000 ppm by weight of nitrogen compounds.

20 The contents of sulfur, oxygen and/or nitrogen compounds often depend on the origin of the feedstock treated. Thus, tyre pyrolysis oils generally contain more heteroelements than plastic pyrolysis oils, in particular sulfur compounds.

The pyrolysis oil can also comprise other impurities, such as heavy metals, for example mercury, arsenic, zinc and lead, for example up to 100 ppb by weight or else 200 ppb by
 25 weight of mercury or of arsenic, and generally between 1 and 200 ppb by weight or between 1 and 100 ppb by weight of heavy metals.

The feedstock of the process according to the invention comprises at least one plastic and/or tyre and/or solid recovered fuel pyrolysis oil, and this in any proportion. Said feedstock can consist solely of pyrolysis oil(s). Preferably, said feedstock comprises at least 50% by weight,
 30 in a preferred way between 70% and 100% by weight, of pyrolysis oil, relative to the total weight of the feedstock, that is to say preferably between 50% and 100% by weight and in a preferred way between 70% and 100% by weight of pyrolysis oil.

The feedstock of the process according to the invention may further comprise, at a low content, typically between 1% and 50% by weight of the feedstock, indeed even between 1%

and 30% or between 1% and 10% by weight, in addition to the pyrolysis oil, a conventional petroleum feedstock or a feedstock resulting from the conversion of biomass which is then co-treated with the pyrolysis oil of the feedstock.

5 The conventional petroleum feedstock can advantageously be a cut or a mixture of cuts of naphtha, gas oil or vacuum gas oil type.

The feedstock resulting from the conversion of biomass can advantageously be chosen from vegetable oils, oils from algae or algal oils, fish oils, waste food oils, and fats of vegetable or animal origin, or mixtures of such feedstocks. Said vegetable oils can advantageously be crude or completely or partly refined, and can be derived from plants chosen from rape,
 10 sunflower, soya, palm, olive, coconut, coconut kernel, castor oil plant and cotton plant, peanut oil, linseed oil and sea kale oil, and all the oils resulting, for example, from sunflower or rape by genetic modification or hybridization, this list not being limiting. Said animal fats are advantageously chosen from pig fat and fats composed of residues from the food industry or resulting from the catering industries. Frying oils, various animal oils, such as fish
 15 oils, tallow or lard, can also be used. The feedstock obtained from the conversion of biomass can also advantageously be chosen from fatty acid methyl esters of vegetable and/or animal origin or else fatty acid methyl esters from waste edible vegetable oils.

The feedstock obtained from the conversion of biomass can also be chosen from feedstocks originating from thermal or catalytic biomass conversion processes, such as oils which are
 20 produced from biomass, in particular from lignocellulosic biomass, with various liquefaction methods, such as hydrothermal liquefaction or pyrolysis. The term "biomass" refers to a material derived from recently living organisms, which comprises plants, animals and by-products thereof. The term "lignocellulosic biomass" denotes biomass derived from plants or from by-products thereof. The lignocellulosic biomass is composed of carbohydrate polymers
 25 (cellulose, hemicellulose) and of an aromatic polymer (lignin).

The feedstock obtained from the conversion of biomass can also advantageously be chosen from feedstocks obtained from the papermaking industry.

Pretreatment step (optional)

30 The process according to the invention may comprise a pretreatment step which can be carried out before or after the prefractionation step a) and upstream of the selective hydrogenation step b).

Thus, according to the embodiment of carrying out the pretreatment before the prefractionation step a), the feedstock comprising a pyrolysis oil can advantageously be pretreated in an optional pretreatment step, in order to obtain a pretreated feedstock which feeds the prefractionation step a).

- 5 According to the embodiment of carrying out the pretreatment after the prefractionation step a), the naphtha cut obtained from the prefractionation step can advantageously be pretreated in an optional pretreatment step, prior to the selective hydrogenation step b), in order to obtain a pretreated naphtha cut which feeds the selective hydrogenation step b).

10 The pretreatment step can also be carried out on at least one heavy cut. When the pretreatment step is carried out on at least one heavy cut, it is carried out independently of the pretreatment step of the naphtha cut.

According to a variant, this optional pretreatment step makes it possible to reduce the amount of contaminants and of solid particles. This optional pretreatment step makes possible in particular the removal of sediments which can be formed as a result of the
15 unstable nature of the pyrolysis oils and/or of a problem of compatibility between two different feedstocks.

Said optional pretreatment step can be implemented by any method known to a person skilled in the art which makes it possible to reduce the amount of contaminants. It can in particular comprise an adsorption step and/or a filtration step and/or a centrifugation step
20 and/or a decantation step and/or an electrostatic separation step and/or a step of washing with an aqueous solution and/or a gas stripping step.

The optional pretreatment step is advantageously implemented at a temperature of between 20 and 400°C, preferably between 40 and 350°C, and at a pressure between 0.15 and 10.0 MPa abs., preferably between 0.2 and 7.0 MPa abs.

25 According to a variant, said optional pretreatment step is implemented in an adsorption section operated in the presence of at least one adsorbent. The adsorbent can be chosen from a zeolite, activated carbon, a clay, a silica or an alumina. Advantageously, said adsorbent comprises less than 1% by weight of metal elements and is preferably devoid of metal elements. Metal elements of the adsorbent should be understood as meaning the
30 elements from groups VIB, VIIB and VIII.

According to another variant, said optional pretreatment step is carried out in a section for washing with an aqueous solution, for example water or an acidic or basic solution, or else with an organic solvent. This washing section may comprise items of equipment for bringing

the feedstock, or the naphtha cut and/or at least one heavy cut which are obtained after the prefractionation, into contact with the aqueous solution and for separating the phases so as to obtain, on the one hand, the pretreated feedstock or a pretreated cut and, on the other hand, the aqueous solution comprising impurities. These items of equipment can include, for example, a stirred reactor, a decanter, a mixer-decanter and/or a cocurrent or countercurrent washing column.

According to another variant, said optional pretreatment step is implemented by filtration. The filtration step makes it possible to remove the inorganic solids, sediments and/or fines contained in the feedstock, or the naphtha cut and/or at least one heavy cut which are obtained after the prefractionation, in particular the metals, metal oxides and metal chlorides. Use is generally made of a filter, the size (for example the diameter or equivalent diameter) of the pores of which is less than 25 μm , preferably less than or equal to 10 μm , even more preferably less than or equal to 5 μm . Use may also be made of a series of filters with various pore sizes, notably a series of filters having decreasing pore sizes in the flow direction of the feedstock. These filtering media are well known for industrial uses. Cartridge filters or self-cleaning filters are suitable, for example.

According to a variant, filtration adjuvants, for example diatomaceous earths, can be used in the filtration system, as seeding, that is to say in suspension in the feedstock or as a precoat (coating) on the filter.

Irrespective of the filters, in particular with adjuvants, it is possible to use two filters in parallel in order to carry out the unclogging and maintenance on one, while the other is in operation.

According to another variant, said optional pretreatment step is carried out by centrifugation, decantation or else by electrostatic separation.

According to another variant, said optional pretreatment step is implemented by gas stripping, thus reducing the content of oxygen in the feedstock. The gas extraction can remove the oxygen (O_2) which may be dissolved in the feedstock, or the naphtha cut and/or at least one heavy cut which are obtained after the prefractionation, thus reducing the probability of formation of free radicals resulting in polymerization in the downstream steps. The process generally involves bringing the feedstock, or the naphtha cut and/or at least one heavy cut which are obtained after the prefractionation, into contact with an extraction gas (for example H_2 , N_2 or a mixture of these), thus transferring at least a portion of the dissolved oxygen from the feedstock or the cut to the extraction gas, followed by the separation of the extraction gas from the feedstock or the cut. Any dissolved H_2 remaining in the feedstock, or the naphtha cut and/or at least one heavy cut which are obtained after the prefractionation,

after the gas extraction step is not a problem, considering the hydrogenation steps carried out downstream.

Said optional pretreatment step generally comprises one or more, preferably several, treatments described above.

5

Prefractionation step a)

The process according to the invention comprises a step a) of prefractionating the feedstock, which is optionally pretreated, in order to obtain a naphtha cut and at least one heavy cut.

10 The term "naphtha cut" is understood to mean a hydrocarbon cut comprising compounds having a boiling point generally below or equal to 175°C, in particular between 45°C and 175°C.

15 The term "heavy cut" is understood to mean a hydrocarbon cut comprising compounds having a boiling point generally above 175°C. The heavy cut can include middle distillates, such as a diesel cut and/or a kerosene cut. It can also comprise heavier compounds, such as a vacuum gas oil (or VGO). The kerosene cut generally has initial and final boiling points in an interval ranging approximately from 175°C to 250°C and the diesel cut generally has initial and final boiling points within an interval ranging approximately from 250°C to 370°C. With regard to the vacuum gas oil cut, it generally has boiling points above 370°C.

20 Depending on the destination or use of the cuts obtained from the prefractionation step, those skilled in the art will adjust the cut points in the stripping and/or distillation operations. For example, it may be necessary to adjust the final point of the naphtha cut to 150°C, 175°C, 180°C or 200°C, indeed even 250°C.

25 The prefractionation step can be carried out so as to obtain a naphtha cut and a (single) heavy cut. It can also be carried out so as to obtain a naphtha cut, a middle distillate cut and a vacuum gas oil cut. The middle distillate cut can, in addition, be fractionated to give a kerosene cut and to give a diesel cut.

The prefractionation step is advantageously carried out at a pressure of less than or equal to 1.0 MPa abs., preferably between 0.1 and 1.0 MPa abs.

30 The prefractionation step can advantageously be carried out by any method known to a person skilled in the art, such as, for example, the combination of one or more separators (drums), and/or one or more stripping columns, and/or a distillation column, it being possible for this or these separator(s) (drum(s)) and/or columns to be optionally fed with a stripping

gas, for example a hydrogen-rich gas stream. Preferably, the prefractionation step uses a distillation column.

The impurities contained in the initial pyrolysis oil are not distributed in the same way in the various cuts after the prefractionation. The naphtha cut generally contains the majority of the diolefins, monoolefins, chlorine compounds and silicon compounds. With regard to the heavy cut, it generally contains very little or nothing in the way of diolefins. In addition, it contains fewer chlorine compounds and silicon compounds than the naphtha cut. However, the sulfur- and/or nitrogen-based impurities are generally concentrated in the heavy cut.

Selective hydrogenation step b)

According to the invention, the process comprises a selective hydrogenation step b) carried out in a reaction section fed with said naphtha cut and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature of between 100°C and 260°C, a hydrogen partial pressure of between 1.0 and 10.0 MPa abs. and an hourly space velocity of between 0.1 and 10.0 h⁻¹, in order to obtain a selectively hydrogenated effluent.

The selective hydrogenation step is carried out under hydrogen pressure and temperature conditions that make it possible to maintain said naphtha cut in the liquid phase and with an amount of soluble hydrogen which is just necessary for a selective hydrogenation of the diolefins present in said naphtha cut. The selective hydrogenation of the diolefins in the liquid phase thus makes it possible to avoid or at least to limit the formation of "gums", that is to say the polymerization of the diolefins and thus the formation of oligomers and polymers, which can plug the reaction section of downstream steps c) and d). Said selective hydrogenation step makes it possible to obtain a selectively hydrogenated effluent, that is to say an effluent with a reduced content of olefins, in particular of diolefins, preferably devoid of diolefins.

Said reaction section implements a selective hydrogenation, preferably in a fixed bed, in the presence of at least one selective hydrogenation catalyst, advantageously at an average temperature between 100°C and 260°C, preferably between 110°C and 250°C, preferably between 120 and 220°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs., preferably between 1.5 and 8.0 MPa abs. and very preferably between 2.0 and 6.0 MPa abs. and at an hourly space velocity (HSV) between 0.1 and 10.0 h⁻¹, preferably between 0.2 and 5.0 h⁻¹, and very preferably between 0.3 and 3.0 h⁻¹.

According to the invention, the "average temperature" of a reaction section corresponds to the weight-average bed temperature (WABT), which is well known to a person skilled in the

art. The average temperature is advantageously determined as a function of the catalytic systems, of the items of equipment, of the configuration of these, that are used. The average temperature (or WABT) is calculated in the following way:

$$WABT = (T_{inlet} + T_{outlet})/2$$

- 5 with T_{inlet} : the temperature of the stream at the inlet of the reaction section and T_{outlet} : the temperature of the effluent at the outlet of the reaction section. Unless otherwise indicated, the “average temperature” of a reaction section is given at cycle beginning conditions.

The hourly space velocity (HSV) is defined here as the ratio of the hourly volume flow rate of the feedstock (here naphtha cut) to the volume of catalyst(s).

- 10 The amount of the gas stream comprising hydrogen (H_2) feeding said reaction section of step b) is advantageously such that the hydrogen coverage is between 1 and 200 Nm^3 of hydrogen per m^3 of feedstock (Nm^3/m^3), preferably between 1 and 150 Nm^3 of hydrogen per m^3 of feedstock (Nm^3/m^3), preferably between 5 and 100 Nm^3 of hydrogen per m^3 of feedstock (Nm^3/m^3).
- 15 The hydrogen coverage is defined as the ratio of the volume flow rate of hydrogen taken under normal temperature and pressure conditions relative to the volume flow rate of the feedstock (here naphtha cut), without taking into account any recycled fraction, at 15°C (in normal m^3 , denoted Nm^3 , of H_2 per m^3 of feedstock).

- The gas stream comprising hydrogen, which feeds the reaction section of step b), may
20 consist of a supply of hydrogen and/or of recycled hydrogen obtained in particular from the separation step e).

- Advantageously, the reaction section of said selective hydrogenation step comprises between 1 and 5 reactors. According to a particular embodiment of the invention, the reaction section comprises between 2 and 5 reactors, which operate in permutable mode,
25 referred to by the term PRS for permutable reactor system or by the term “lead and lag”. The combination of at least two reactors in PRS mode makes it possible to isolate a reactor, to discharge the spent catalyst, to recharge the reactor with fresh catalyst and to bring said reactor back into service without shutting down the process. The PRS technology is described in particular in patent FR2681871.

- 30 Advantageously, reactor internals, for example of filter plate type, can be used to prevent the plugging of the reactor(s). An example of a filter plate is described in patent FR 3051375.

Advantageously, said at least one selective hydrogenation catalyst comprises a support, preferably a mineral support, and a hydrodehydrogenating function.

The hydrodehydrogenating function comprises in particular at least one element from Group VIII, preferably chosen from nickel and cobalt, and/or at least one element from Group VIb, preferably chosen from molybdenum and tungsten. The total content of oxides of metallic elements from groups VIB and VIII (that is to say the sum of the metallic elements from groups VIB and VIII) is preferably between 1% and 40% by weight and preferentially from 5% to 30% by weight relative to the total weight of the catalyst. The ratio by weight, expressed as metal oxide, of the metal (or metals) from group VIB relative to the metal (or to the metals) from group VIII is preferably between 1 and 20 and with preference between 2 and 10. For example, the selective hydrogenation catalyst comprises between 0.5% and 10% by weight of nickel, preferably between 1% and 5% by weight of nickel (expressed as nickel oxide NiO relative to the weight of said catalyst), and between 1% and 30% by weight of molybdenum, preferably between 3% and 20% by weight of molybdenum (expressed as molybdenum oxide MoO₃ relative to the weight of said catalyst), on a preferably mineral support.

The support for said at least one selective hydrogenation catalyst is preferably chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof. Said support can include dopant compounds, in particular oxides chosen from boron oxide, especially boron trioxide, zirconia, ceria, titanium oxide, phosphorus pentoxide and a mixture of these oxides. Preferably, said selective hydrogenation catalyst comprises an alumina support, preferably doped with phosphorus and optionally boron. When phosphorus pentoxide P₂O₅ is present, its concentration is less than 10% by weight, relative to the weight of the alumina, and advantageously at least 0.001% by weight, relative to the total weight of the alumina. When boron trioxide B₂O₃ is present, its concentration is less than 10% by weight relative to the weight of the alumina, and advantageously at least 0.001% relative to the total weight of the alumina. The alumina used may be, for example, a γ (gamma) or η (eta) alumina.

Said selective hydrogenation catalyst is, for example, in the form of extrudates.

According to another aspect of the invention, the selective hydrogenation catalyst as described above additionally comprises one or more organic compounds containing oxygen and/or nitrogen and/or sulfur. Such a catalyst is often denoted by the term "additivated catalyst". Generally, the organic compound is chosen from a compound comprising one or more chemical functions chosen from a carboxylic, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function or else compounds including a furan ring or else sugars.

Preferably, the selective hydrogenation step can employ, upstream of the selective hydrogenation catalyst(s), at least one guard bed containing adsorbents of alumina, silica-alumina, zeolite and/or activated carbon type optionally containing metals from group VIB and/or VIII in the selective hydrogenation section. Use may also be made of a series of guard
 5 beds with particles of different diameters, notably a series of guard beds having decreasing diameters in the flow direction of the feedstock (also referred to as "grading").

The content of impurities, in particular of diolefins, of the selectively hydrogenated effluent obtained on conclusion of the selective hydrogenation step is reduced with respect to that of the same impurities, in particular of the diolefins, included in the naphtha cut obtained after
 10 the prefractionation. The selective hydrogenation step a) makes it possible to convert at least 60% and preferably at least 70% of the diolefins contained in the naphtha cut. The selectively hydrogenated effluent, obtained on conclusion of selective hydrogenation step b), is sent at least in part and preferably entirely, preferably directly, to the hydrogenation step c).

15 **Hydrogenation step c)**

According to the invention, the process comprises a hydrogenation step c) carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one
 20 hydrogenation catalyst, said hydrogenation reaction section being fed at least with said selectively hydrogenated effluent obtained from step b) and a gas stream comprising hydrogen, said hydrogenation reaction section being employed at an average temperature between 180°C and 380°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrogenated effluent.

Step c) is carried out in particular under temperature and hydrogen pressure conditions which
 25 make it possible to carry out the hydrodemetallization of at least one portion of the metals, in particular the retention of silicon, and the hydrodechlorination by removing at least one portion, and preferably all, of the chlorine. It also makes it possible to hydrogenate the monoolefins. This step makes it possible to limit the catalyst deactivation of the reaction section of the downstream hydrotreating step d) when it is present.

30 A person skilled in the art will readily understand that, in the hydrogenation step c), hydrogenation reactions as described above are carried out and at the same time also some of the other hydrotreating reactions, and in particular hydrodesulfurization and hydrodenitrogenation reactions, even if these reactions are instead favoured in the hydrotreating step d), which is generally carried out at a higher temperature.

Said reaction section carries out a hydrogenation in the presence of at least one hydrogenation catalyst, advantageously at an average temperature (or WABT as defined below) between 180°C and 380°C, preferably between 200°C and 350°C and particularly preferably between 240°C and 330°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs., preferably between 1.5 and 8.0 MPa abs. and very preferably between 2.0 and 6.0 MPa abs., and at an hourly space velocity (HSV) between 0.1 and 10.0 h⁻¹, preferably between 0.2 and 5.0 h⁻¹ and very preferably between 0.3 and 3.0 h⁻¹. The amount of the gas stream comprising hydrogen (H₂) feeding said reaction section is advantageously such that the hydrogen coverage is between 100 and 1500 Nm³ of hydrogen per m³ of feedstock (Nm³/m³), preferably between 120 and 1000 Nm³ of hydrogen per m³ of feedstock (Nm³/m³), preferably between 150 and 800 Nm³ of hydrogen per m³ of feedstock (Nm³/m³). The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above in step b).

Advantageously, the reaction section of said step c) comprises between 1 and 5 reactors, preferably between 2 and 5 reactors, and particularly preferably it comprises two reactors. Each reactor comprises at least one catalyst bed, for example between 1 and 10 catalyst beds.

According to a particularly preferred alternative form, the hydrogenation reaction section of step c) comprises two reactors operating in permutable (PRS) mode as described above.

Advantageously, reactor internals, for example of filter plate type, can be used to prevent the plugging of the reactor(s). An example of a filter plate is described in patent FR 3051375.

Advantageously, said hydrogenation catalyst comprises a support, preferably an inorganic support, and a hydrogenating-dehydrogenating function.

According to one variant, the hydrogenating-dehydrogenating function comprises in particular at least one group VIII element, preferably chosen from nickel and cobalt, and at least one group VIB element, preferably chosen from molybdenum and tungsten. According to this variant, the total content, expressed as oxides, of the metal elements from groups VIB and VIII is preferably between 1% and 40% by weight, preferentially from 5% to 30% by weight, relative to the total weight of the catalyst. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively. When the metal is molybdenum or tungsten, the metal content is expressed as MoO₃ and WO₃ respectively.

The ratio by weight, expressed as metal oxide, of the group VIB metal(s) relative to the group VIII metal(s) is preferably between 1 and 20 and preferably between 2 and 10.

According to this variant, the reaction section of said step c) comprises, for example, a hydrogenation catalyst comprising between 0.5% and 12% by weight of nickel, preferably between 0.9% and 10% by weight of nickel (expressed as nickel oxide NiO relative to the weight of said catalyst), and between 1% and 30% by weight of molybdenum, preferably
 5 between 3% and 20% by weight of molybdenum (expressed as molybdenum oxide MoO₃ relative to the weight of said catalyst), on a preferably inorganic support, preferably on an alumina support.

According to another variant, the hydrogenating-dehydrogenating function comprises, and preferably consists of, at least one group VIII element, preferably nickel. According to this
 10 variant, the content of nickel oxides is preferably between 1% and 50% by weight, preferably between 10% and 30% by weight, relative to the weight of said catalyst. This type of catalyst is preferably used in its reduced form, on a preferably mineral support, preferably on an alumina support.

The support of said hydrogenation catalyst is preferably chosen from alumina, silica, silicas-
 15 aluminas, magnesia, clays and mixtures thereof. Said support can include dopant compounds, in particular oxides chosen from boron oxide, especially boron trioxide, zirconia, ceria, titanium oxide, phosphorus pentoxide and a mixture of these oxides. Preferably, said hydrogenation catalyst comprises an alumina support, optionally doped with phosphorus and optionally boron. When phosphorus pentoxide P₂O₅ is present, its concentration is less than
 20 10% by weight, relative to the weight of the alumina, and advantageously at least 0.001% by weight, relative to the total weight of the alumina. When boron trioxide B₂O₃ is present, its concentration is less than 10% by weight, relative to the weight of the alumina, and advantageously at least 0.001%, relative to the total weight of the alumina. The alumina used may be, for example, a γ (gamma) or η (eta) alumina.

25 Said hydrogenation catalyst is, for example, in the form of extrudates.

Very preferably, step c) can employ, in addition to the hydrogenation catalyst(s) described above, moreover at least one hydrogenation catalyst used in step c) comprising less than 1% by weight of nickel and at least 0.1% by weight of nickel, preferably 0.5% by weight of nickel, expressed as nickel oxide NiO relative to the weight of said catalyst, and less than 5% by
 30 weight of molybdenum and at least 0.1% by weight of molybdenum, preferably 0.5% by weight of molybdenum, expressed as molybdenum oxide MoO₃ relative to the weight of said catalyst, on an alumina support. This catalyst, not highly loaded with metals, can be preferably placed upstream or downstream of the hydrogenation catalyst(s) described above, preferably upstream.

According to another aspect of the invention, the hydrogenation catalyst as described above additionally comprises one or more organic compounds containing oxygen and/or nitrogen and/or sulfur as described above (additivated catalyst).

5 Preferably, step c) can employ, upstream of the hydrogenation catalyst(s), at least one guard bed or a series of guard beds of "grading" type as described above for step b).

According to a particular embodiment, all or part of the feedstock (naphtha cut) can be injected in stages at the inlet of each catalyst bed so as to manage the exotherms, as described in FR2969642. In this case, the total stream of the feedstock (naphtha cut) is divided into a certain number of different partial streams equal to the number of catalyst beds
10 in the reactor, the different partial streams being injected at the inlets of the successive catalyst beds in increasing proportions.

In order to control the highly exothermic reactions in this reaction section, a liquid and/or gaseous diluent can be injected in step c) (also referred to as quench). This makes it possible, on the one hand, to dilute the impurities and, on the other hand, to control the
15 temperature.

The temperature difference (ΔT) between the outlet and inlet of each catalyst bed of the hydrogenation step c) is generally less than 30°C, indeed even less than 25°C.

The injection of the liquid and/or gaseous diluent can be carried out at the first catalyst bed of the reaction section, or between the various catalyst beds of each section. When the reaction
20 section comprises two reactors operating in permutable mode, at least one portion of the liquid and/or gaseous diluent can be injected between the two reactors.

The liquid diluent (or liquid quench) can be an external liquid (for example a fossil naphtha cut) or a liquid internal to the process. Preferably, the liquid diluent is a portion of the naphtha cut obtained in step e) (recycle).

25 Advantageously, when the diluent is liquid, the amount of liquid diluent injected is adjusted so that the weight ratio of the liquid diluent stream to the feedstock (naphtha cut) is less than or equal to 10, preferably less than or equal to 7, and preferentially greater than or equal to 0.001, preferably greater than or equal to 0.01 and preferably greater than or equal to 0.1. Preferably, the amount of liquid diluent is adjusted so that the weight ratio of the liquid
30 diluent stream to the feedstock is between 0.01 and 10, preferably between 0.1 and 7, and particularly preferably between 0.2 and 5.

This ratio makes it possible in particular to control the rise in temperature in step c). This is because, when the ratio is high, the rate of dilution of the feedstock is high, and the rise in temperature at the beginning of the reaction section of step c), in particular due to the monoolefin hydrogenation reactions, is thus controllable by the dilution effect.

- 5 The gaseous diluent (or gaseous quench) is generally a gas stream comprising fresh and/or recycled hydrogen. Preferably, the gaseous diluent is at least one portion of the gaseous effluent obtained in step e) which contains hydrogen, which is optionally purified.

Advantageously, when the diluent is gaseous, the amount of gaseous diluent injected is adjusted so that the hydrogen coverage is between 100 and 1500 Nm³ of hydrogen per m³ of feedstock (Nm³/m³), preferably between 120 and 1000 Nm³ of hydrogen per m³ of feedstock (Nm³/m³), preferably between 150 and 800 Nm³ of hydrogen per m³ of feedstock (Nm³/m³).

The liquid and/or gaseous diluent can also be injected in the same way in step b) and/or d) in order to control the exotherm.

Said hydrogenation step c) makes it possible to obtain a hydrogenated effluent, that is to say an effluent having a reduced content of metals, in particular of silicon and of halogens, in particular of chlorine. It also makes it possible to hydrogenate the monoolefins. Step c) generally makes it possible to convert at least 40% and preferably at least 60% of the monoolefins contained in the naphtha cut. Preferably, at least 50% and more preferentially at least 75% of the chlorine and silicon of the initial feedstock are respectively removed during step c). Generally, the silicon content is less than 10 ppm by weight in the hydrogenated effluent of step c).

Depending on the content of residual impurities in the hydrogenated naphtha cut obtained after step c) and its final destination, this cut can be subjected to a hydrotreating step. When it is desired to use this cut as a feedstock for a steam cracker to produce olefins, a hydrotreating step is generally necessary in order to achieve the sulfur and nitrogen specifications. In this case, the effluent obtained on conclusion of step c) is sent, at least partly and preferably completely, preferably directly, to the hydrotreating step d).

When it is desired to send this cut to a fuel storage unit, a hydrotreating step may not be necessary. In this case, the effluent obtained on conclusion of step c) is sent, at least partly and preferably completely, preferably directly, to the separation step e).

Hydrotreating step c) (optional)

According to the invention, the process may comprise a hydrotreating step d) carried out in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one

5 hydrotreating catalyst, said hydrotreating reaction section being fed at least with said hydrogenated effluent resulting from step c) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an average temperature between 200°C and 400°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrotreated effluent.

10 Advantageously, step d) carries out hydrotreating reactions well known to a person skilled in the art and more particularly hydrotreating reactions such as the hydrogenation of aromatics, hydrodesulfurization and hydrodenitrogenation. In addition, the hydrogenation of the remaining olefins and halogen compounds and also the hydrodemetallization can continue even if most and preferably all of these impurities were removed during step c).

15 Said hydrotreating reaction section is advantageously implemented at an average hydrotreating temperature between 200°C and 400°C, preferably between 250°C and 360°C, at a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and at an hourly space velocity (HSV) between 0.1 and 10.0 h⁻¹, preferably between 0.1 and 5.0 h⁻¹, preferentially between 0.2 and 2.0 h⁻¹, preferably between 0.2 and 1 h⁻¹. The hydrogen coverage in step d)
20 is advantageously of between 100 and 1500 Nm³ of hydrogen per m³ of the feedstock which feeds step d), and preferably between 120 and 1000 Nm³/m³, preferably between 150 and 800 Nm³/m³. The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above.

25 Compared with the processes for treating a feedstock comprising a pyrolysis oil which treat all of the pyrolysis oil (without prefractionation), the operating conditions of the hydrogenation step and also those of the hydrotreating step can be milder in the process according to the invention (in particular a lower temperature and/or a higher HSV). This is because the sulfur-containing and nitrogen-containing impurities, in particular the most refractory, are found after the prefractionation predominantly in said heavy cut.

30 Advantageously, the reaction section of said step d) comprises between 1 and 5 reactors, preferably between 2 and 5 reactors. These reactors can operate in series and/or in parallel and/or in permutable (or PRS) mode.

In a preferred embodiment, said hydrotreating reaction section comprises a single fixed-bed reactor containing n catalyst beds, n being an integer greater than or equal to one, preferably between one and ten, preferably between two and five. In a particularly preferred embodiment, the hydrogenation reaction section of step c) comprises two reactors operating in permutable mode, followed by the hydrotreating reaction section of step d) which comprises a single fixed-bed reactor.

In another embodiment, said hydrogenation reaction section and said hydrotreating section may be in a single (sole) fixed-bed reactor containing n catalyst beds, n being an integer greater than or equal to one, preferably between one and ten, preferably between two and seven. In this case, the naphtha cut passes first through the hydrogenation reaction section and then the hydrotreating section.

In another embodiment, it is possible to have at least two reactors, preferably between 2 and 5 reactors, operating in permutable (PRS) mode, each reactor containing a hydrogenation reaction section and then a hydrotreating section.

Advantageously, reactor internals, for example of filter plate type, can be used to prevent the plugging of the reactor(s).

Advantageously, said hydrotreating catalyst used in said step d) can be chosen from known hydrodemetallization, hydrotreating or silicon-scavenging catalysts, used in particular for the treatment of petroleum cuts, and combinations thereof. Known hydrodemetallization catalysts are, for example, those described in Patents EP 0113297, EP 0113284, US 5221656, US 5827421, US 7119045, US 5622616 and US 5089463. Known hydrotreating catalysts are, for example, those described in Patents EP 0113297, EP 0113284, US 6589908, US 4818743 or US 6332976. Known silicon-scavenging catalysts are, for example, those described in patent applications CN 102051202 and US 2007/080099.

In particular, said hydrotreating catalyst comprises a support, preferably an inorganic support, and at least one metal element having a hydrogenating-dehydrogenating function. Said metal element having a hydrogenating-dehydrogenating 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, expressed as oxides, of the metal elements from groups VIB and VIII is preferably between 0.1% and 40% by weight, preferentially from 5% to 35% by weight, with respect to the total weight of the catalyst. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively. When the metal is molybdenum or tungsten, the metal content is expressed as

MoO₃ and WO₃ respectively. The ratio by weight, expressed as metal oxide, of the metal (or metals) from group VIB, relative to the metal (or metals) from group VIII, is preferably of between 1.0 and 20, in a preferred way between 2.0 and 10. For example, the hydrotreating reaction section of step d) of the process comprises a hydrotreating catalyst comprising
 5 between 0.5% and 10% by weight of nickel, preferably between 1% and 8% by weight of nickel, expressed as nickel oxide NiO, with respect to the total weight of the hydrotreating catalyst, and between 1.0% and 30% by weight of molybdenum, preferably between 3.0% and 29% by weight of molybdenum, expressed as molybdenum oxide MoO₃, with respect to the total weight of the hydrotreating catalyst, on an inorganic support, preferably on an
 10 alumina support.

The support of said hydrotreating catalyst is advantageously chosen from alumina, silica, silicas-aluminas, magnesia, clays and mixtures thereof. Said support can additionally include dopant compounds, in particular oxides chosen from boron oxide, especially boron trioxide, zirconia, ceria, titanium oxide, phosphorus pentoxide and a mixture of these oxides.

15 Preferably, said hydrotreating catalyst comprises an alumina support, preferably an alumina support doped with phosphorus and optionally boron. When phosphorus pentoxide P₂O₅ is present, its concentration is less than 10% by weight, relative to the weight of the alumina, and advantageously at least 0.001% by weight, relative to the total weight of the alumina. When boron trioxide B₂O₃ is present, its concentration is less than 10% by weight, relative to
 20 the weight of the alumina, and advantageously at least 0.001%, relative to the total weight of the alumina. The alumina used can, for example, be a γ (gamma) or η (eta) alumina.

Said hydrotreating catalyst is, for example, in the form of extrudates.

Advantageously, said hydrotreating catalyst of the process has a specific surface area of greater than or equal to 250 m²/g, preferably greater than or equal to 300 m²/g. The specific
 25 surface area of said hydrotreating catalyst is advantageously of less than or equal to 800 m²/g, preferably of less than or equal to 600 m²/g, in particular of less than or equal to 400 m²/g. The specific surface area of the hydrotreating catalyst is measured by the BET method, that is to say the specific surface area determined by nitrogen adsorption in accordance with the standard ASTM D 3663-78 drawn up from the Brunauer-Emmett-Teller method described
 30 in the periodical *The Journal of the American Chemical Society*, 6Q, 309 (1938). Such a specific surface area makes it possible to further improve the removal of the contaminants, in particular of the metals, such as silicon.

According to another aspect of the invention, the hydrotreating catalyst as described above additionally comprises one or more organic compounds containing oxygen and/or nitrogen
 35 and/or sulfur as described above (additivated catalyst).

Preferably, step d) can employ, upstream of the hydrotreating catalyst(s), at least one guard bed or a series of guard beds of "grading" type as described above for step b).

Advantageously, the hydrotreating step c) makes possible the hydrogenation of at least 80% and preferably of all of the remaining olefins and halogen compounds after the hydrogenation step c), but also the at least partial conversion of other impurities present in the feedstock, such as aromatic compounds, metal compounds, sulfur compounds, nitrogen compounds or oxygen compounds. Preferably, the nitrogen content at the outlet of step d) is less than 100 ppm by weight and preferably less than 10 ppm by weight. Preferably, the sulfur content at the outlet of step d) is less than 100 ppm by weight, and preferably less than 10 ppm by weight. Step d) can also make it possible to further reduce the content of contaminants, such as that of metals, in particular the silicon content. With preference, the metal content at the outlet of step d) is less than 10 ppm by weight and preferably less than 2 ppm by weight, and the silicon content is less than 5 ppm by weight. Preferably, the content of halogen element at the outlet of step d) is less than 5 ppm by weight.

The hydrotreated effluent obtained from the hydrotreating step d) is then sent, partly or completely, to a separation step e).

Any reaction section of steps b) and c) and d) is advantageously fed at the first catalyst bed of the first reactor in operation. An injection of at least a portion of the feedstock and/or at least a portion of hydrogen between the various catalytic beds is also possible.

Any reaction section of steps b) and c) and d) employing at least one fixed-bed reactor can operate with gas and liquid downflow or upflow.

The gas stream comprising hydrogen, which feeds at least one reaction section of steps b) and c) and d) can consist of makeup hydrogen and/or of recycled hydrogen and/or of hydrogen originating from the upstream step. The gas stream comprising hydrogen may be derived from a fossil source or from a renewable source, for example derived from the gasification of plastic waste, or produced by electrolysis.

Preferably, an additional gas stream (gaseous quench) comprising hydrogen is advantageously introduced at the inlet of each reactor, in particular operating in series, and/or at the inlet of each catalyst bed starting from the second catalyst bed of the reaction section.

The preparation of the catalysts of steps b) and c) and d) is known and generally comprises a step of impregnation of metals from group VIII and from group VIB, when present, and optionally of phosphorus and/or of boron on the support, followed by drying, and then

optionally by a calcination. In the case of additivated catalyst, the preparation generally takes place by simple drying without calcination after introduction of the organic compound. The term "calcination" is understood here to mean a heat treatment under a gas containing air or oxygen at a temperature above or equal to 200°C. Before being used in a step of the process, the catalysts are generally subjected to a sulfidation in order to form the active species. When the catalyst is a catalyst used in its reduced form, the preparation involves a reduction step.

Depending on the content of sulfur compounds in the initial feedstock to be treated, a stream containing a sulfiding agent can be injected upstream of the optional pretreatment step and/or the hydrogenation step and/or the optional hydrotreating step, preferably upstream of the hydrogenation step and/or the hydrotreating step, in order to ensure a sufficient amount of sulfur to form the active species of the catalyst (in sulfide form).

This activation or sulfidation step is carried out by methods well known to a person skilled in the art, and advantageously under a sulfo-reductive atmosphere in the presence of hydrogen and hydrogen sulfide. The sulfiding agents are preferably H₂S gas, elemental sulfur, CS₂, mercaptans, sulfides and/or polysulfides, hydrocarbon cuts having a boiling point below 400°C containing sulfur compounds or any other sulfur-containing compound used for the activation of hydrocarbon feedstocks with a view to sulfiding the catalyst. Said sulfur-containing compounds are advantageously chosen from alkyl disulfides, such as, for example, dimethyl disulfide (DMDS), alkyl sulfides, such as, for example, dimethyl sulfide, thiols, such as, for example, n-butyl mercaptan (or 1-butanethiol), and polysulfide compounds of tert-nonyl polysulfide type. The catalyst can also be sulfided by the sulfur contained in the feedstock to be desulfurized. Preferably, the catalyst is sulfided *in situ* in the presence of a sulfiding agent and of a hydrocarbon feedstock. Very preferably, the catalyst is sulfided *in situ* in the presence of the feedstock additivated with dimethyl disulfide. The injection of a sulfiding agent is in particular necessary at the start of the catalytic cycle, while the H₂S is formed. Additional injections throughout the catalytic cycle may be necessary in order to compensate for the natural loss.

Washing/separation step e)

According to the invention, the process comprises a separation step e), fed with the hydrogenated effluent obtained from step c) or with the hydrotreated effluent obtained from step d) and an aqueous solution, said step being carried out in a separation section at a temperature between 30°C and 300°C, in order to obtain at least a gaseous effluent, an aqueous effluent and a naphtha cut stripped of its impurities.

This washing/separation step makes it possible in particular to remove ammonium chloride salts, which are formed by reaction between chloride ions, released by hydrogenation of chlorine compounds in the form of HCl, notably during the hydrogenation step, followed by dissolution in water, and ammonium ions, generated notably by the hydrogenation of nitrogen compounds in the form of NH_3 during the hydrogenation and/or hydrotreating step and/or supplied by injection of an amine, followed by dissolution in water, and thus to limit the risks of clogging, in particular in the transfer lines and/or in the sections of the process of the invention and/or the transfer lines to the steam cracker, due to the precipitation of the ammonium chloride salts. This step also makes it possible to remove the hydrochloric acid formed by the reaction of the hydrogen ions and the halide ions released by hydrogenation of the halogen compounds during the hydrogenation step which dissolve in the aqueous solution. When H_2S is formed, the washing/separation step also makes it possible to remove ammonium sulfide salts ($(\text{NH}_4)_2\text{S}$) which are formed by reaction between the H_2S resulting from the hydrodesulfurization of the sulfur compounds and the NH_3 by dissolving them in the aqueous solution.

The washing/separation step is advantageously carried out at a temperature of between 20°C and 300°C , preferentially between 25°C and 200°C , preferably between 30°C and 150°C and particularly preferably between 30°C and 100°C . Advantageously, the washing/separation step is carried out at a pressure close to that employed in the hydrotreating step, preferably between 1.0 and 10.0 MPa abs., so as to facilitate the recycling of hydrogen.

The aqueous solution may be water. It can also be a basic aqueous solution (by addition of NaOH, for example). The use of a basic solution makes it possible to neutralize the hydrogen halides and any dissolved salts.

Said separation section can comprise any separation means known to a person skilled in the art, in particular one or more knockout drums 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. The washing/separation step can advantageously be carried out in common or separate items of washing and separation equipment, these items of equipment being well known (separator drums which can be operated at various pressures and temperatures, pumps, heat exchangers, washing columns, and the like).

Advantageously, the washing/separation step comprises an injection of an aqueous solution, preferably an injection of water, into the hydrogenated or hydrotreated effluent, upstream of

the washing/separation section, so as to dissolve at least in part and preferably all of the hydrogen halides (HCl in particular) and any salts present.

In an optional embodiment of the invention, the washing/separation step comprises the injection of an aqueous solution into the hydrogenated or hydrotreated effluent, followed by
 5 the washing/separation section advantageously comprising a separation phase which makes it possible to obtain at least one aqueous effluent charged with hydrogen halides (HCl in particular) and possible dissolved salts, said naphtha cut stripped of these impurities and a partially washed gaseous effluent. Said aqueous effluent and the washed naphtha cut can subsequently be separated in a decanting vessel in order to obtain said washed naphtha cut
 10 and said aqueous effluent. Said partially washed gaseous effluent can, in parallel, be introduced into a washing column where it circulates countercurrentwise to an aqueous stream, preferably of the same nature as the aqueous solution injected into the hydrotreated effluent, which makes it possible to remove at least some and preferably all of the hydrochloric acid contained in the partially washed gaseous effluent and to thus obtain said
 15 gaseous effluent, preferably essentially comprising hydrogen, and an acidic aqueous stream. Said aqueous effluent obtained from the decanting vessel may optionally be mixed with said acidic aqueous stream, and be used, optionally as a mixture with said acidic aqueous stream, in a water recycling circuit to feed the washing/separation step with said aqueous solution upstream of the washing/separation section and/or with said aqueous stream in the
 20 washing column. Said water recycling circuit can comprise a supply of water and/or of a basic solution and/or a bleed making it possible to discharge the impurities.

According to one embodiment, and depending on the content of chlorine compounds in said naphtha cut obtained after the prefractionation, a stream containing a nitrogen compound such as ammonia or an amine, for example monoethanolamine, diethanolamine,
 25 monodiethanolamine and/or aniline can be injected upstream of the selective hydrogenation step and/or upstream of the hydrogenation step and/or upstream of the hydrotreating step so as to ensure a sufficient amount of ammonium ions for combining the chloride ions formed during the hydrotreating step in the form of ammonium chloride salts, thus making it possible to limit the formation of hydrochloric acid and thus to limit the corrosion downstream of the
 30 separation section.

Said gaseous effluent obtained on conclusion of the washing/separation step advantageously comprises hydrogen, preferably comprises at least 60% by volume, preferably at least 70% by volume, of hydrogen. Said gaseous effluent obtained on conclusion of the washing/separation step contains very little chlorine, generally at a content
 35 of less than 3 ppm by weight of chlorine, which enables it to be sent into a refining unit

requiring hydrogen. According to one embodiment, said gaseous effluent can at least partly be recycled to one of the steps of the process according to the invention requiring hydrogen (steps b), c) and/or d)), it being possible for the recycling system to comprise a purification section (for example for adsorption of heavy metals, such as mercury).

- 5 The aqueous effluent obtained on conclusion of the washing/separation step advantageously comprises ammonium salts and/or hydrochloric acid.

After the separation of the gaseous effluent, said naphtha cut, stripped of its impurities and washed, is preferentially sent to a steam stripping step preferably operating at a pressure of between 0.5 and 2 MPa abs. in order to carry out a separation of the hydrogen sulfide (H₂S)
10 dissolved in said naphtha cut stripped of its impurities.

A portion of said naphtha cut obtained from step e) can be recycled within the hydrogenation step, and optionally within the hydrotreating step in order to constitute a liquid recycle or a quench enabling the exotherms to be controlled.

According to a variant, a portion or all of said naphtha cut obtained from step e) and recycled
15 to the hydrogenation and/or hydrotreating step can be advantageously either cooled, or preheated, if necessary, or kept at the same temperature. The temperature modifications of all or part of said recycled naphtha cut will be performed by any means known to a person skilled in the art (exchanger, cooling tower, furnace, and the like) and will make it possible to adjust the temperature profile (inlet temperature, delta T) of the catalyst beds of the
20 hydrogenation and/or hydrotreating steps as needed.

According to another embodiment, said naphtha cut stripped of its impurities can also be sent, partly or entirely, to a fuel storage unit, for example a unit for storing naphtha, obtained from conventional petroleum feedstocks.

According to another embodiment, which is preferred, said naphtha cut stripped of its
25 impurities is partly and preferably entirely sent directly to the inlet of a steam cracking unit.

Advantageously, the process according to the invention enables the hydrogenation of at least 80% and preferably of all of the olefins (monoolefins and diolefins), but also the conversion, at least in part, of other impurities present in said naphtha cut obtained after the prefractionation, such as aromatic compounds, metal compounds, sulfur compounds,
30 nitrogen compounds, halogen compounds (in particular chlorine compounds) or oxygen compounds.

Preferably, said naphtha cut obtained after separation step e) has a nitrogen content of less than 10 ppm by weight, preferably less than 5 ppm by weight.

Preferably, said naphtha cut obtained after separation step e) has a sulfur content of less than 10 ppm by weight.

- 5 Preferably, said naphtha cut obtained after separation step e) has an oxygen content of less than 10 ppm by weight.

Preferably, said naphtha cut obtained after separation step e) has a metal content of less than 10 ppm by weight, preferably less than 2 ppm by weight, and the silicon content is less than 5 ppm by weight.

- 10 Preferably, said naphtha cut obtained after the separation step e) has a halogen content (in particular chlorine content) of less than 3 ppm by weight.

The contents are given as relative concentrations by weight, percentages (%) by weight, part(s) per million (ppm) by weight or part(s) per billion (ppb) by weight, relative to the total weight of the stream under consideration.

15

Steam cracking step (optional)

Said naphtha cut stripped of its impurities obtained from step e) can be sent, partly or entirely, to a steam cracking step, optionally mixed with a fossil feedstock suitable for the steam cracker.

- 20 Said steam cracking step is advantageously carried out in at least one pyrolysis furnace at a temperature of between 700°C and 900°C, preferably between 750°C and 850°C, and at a pressure of between 0.05 and 0.3 MPa relative. The residence time of the hydrocarbon compounds is generally less than or equal to 1.0 second (denoted s), preferably of between 0.1 and 0.5 s. Advantageously, steam is introduced upstream of the steam cracking step and
- 25 after the separation (or the fractionation). The amount of water introduced, advantageously in the form of steam, is advantageously between 0.3 and 3.0 kg of water per kg of hydrocarbon compounds at the inlet of the steam cracking step. Preferably, the steam cracking step is carried out in several pyrolysis furnaces in parallel, so as to adapt the operating conditions to the various streams, and also to manage the decoking times of the tubes. A furnace
- 30 comprises one or more tubes arranged in parallel. A furnace can also denote a group of furnaces operating in parallel. For example, one furnace may be dedicated to the cracking of the naphtha cut and another dedicated to the middle distillate cut.

The effluents from the various steam cracking furnaces are generally recombined before separation for the purpose of constituting an effluent. It is understood that the steam cracking

step includes the steam cracking furnaces but also the substeps associated with the steam cracking that are well known to a person skilled in the art. These substeps may notably include heat exchangers, columns and catalytic reactors and recycling to the furnaces. A column generally makes it possible to fractionate the effluent for the purpose of recovering at least a light fraction comprising hydrogen and compounds having from 2 to 5 carbon atoms, and a fraction comprising pyrolysis petrol, and optionally a heavier fraction. Columns make it possible to separate the various constituents of the fractionation light fraction in order to recover at least a cut rich in ethylene (C2 cut) and a cut rich in propylene (C3 cut) and optionally a cut rich in butenes (C4 cut). The catalytic reactors make it possible in particular to carry out hydrogenations of the C2, C3, and even C4, cuts and of the pyrolysis petrol. The saturated compounds, notably the saturated compounds having from 2 to 4 carbon atoms, are advantageously recycled to the steam cracking furnaces so as to increase the overall yields of olefins.

This steam cracking step makes it possible to obtain at least one effluent containing olefins comprising 2, 3 and/or 4 carbon atoms (that is to say C2, C3 and/or C4 olefins), at satisfactory contents, in particular of greater than or equal to 30% by weight, notably of greater than or equal to 40% by weight, indeed even of greater than or equal to 50% by weight of total olefins comprising 2, 3 and 4 carbon atoms, relative to the weight of the steam cracking effluent under consideration. Said C2, C3 and C4 olefins can subsequently be advantageously used as polyolefin monomers.

Upgrading of the heavy cut

One or more steps of subsequent treatment of the heavy cut, or of the other cut(s) obtained from the heavy cut during the prefractionation step a) (middle distillate cut including a diesel cut and a kerosene cut, vacuum gas oil cut) other than the naphtha cut, can be carried out in order to upgrade them.

Such a step may comprise at least one step chosen from the list consisting of hydrotreating, steam cracking, hydrocracking and fluid catalytic cracking. These examples of subsequent treatment are not exhaustive.

The subsequent treatment steps can be carried out on a single cut or several of the cuts resulting from the prefractionation step a) as a mixture, alone or as a mixture with a petroleum feedstock and/or a feedstock resulting from the conversion of biomass.

Hydrotreating

In view of the impurities contained in the heavy cut or in the other cut(s) resulting from the heavy cut during the prefractionation step a), a hydrotreating is generally necessary before being able to send the cut(s) either to other subsequent treatments, or to a storage unit, in order to protect the catalysts of subsequent treatments or to meet the required specifications.

- 5 The hydrotreating can be carried out on the (whole) heavy cut or on the middle distillate cut, including a diesel cut and a kerosene cut, or on the vacuum gas oil cut resulting from the prefractionation step a), alone or as a mixture.

It is also possible to carry out a co-processing by mixing the heavy cut, or the other cut(s) resulting from the heavy cut, with a petroleum feedstock and/or a feedstock resulting from the conversion of biomass. Such feedstocks are petrols, gas oils, vacuum gas oils,
 10 atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuel oils, oils, waxes and paraffins, waste oils, deasphalted residues or crudes, feedstocks originating from thermal or catalytic conversion processes, lignocellulosic feedstocks or, more generally, feedstocks resulting from biomass, such as vegetable oils, oils from algae or
 15 algal oils, fish oils, waste edible oils, and fats of vegetable or animal origin, taken alone or as a mixture.

According to a first embodiment, the (whole) heavy cut resulting from the prefractionation step is subjected to a hydrotreating step carried out in a hydrotreating section, preferably in a fixed bed, which is carried out under the operating conditions and with hydrotreating catalysts
 20 as described for the step d) of hydrotreating the naphtha cut.

According to a second embodiment, it is possible to carry out a hydrotreating dedicated to each cut, in particular a hydrotreating dedicated to the middle distillate cut (including a diesel cut or a kerosene cut) and/or a hydrotreating dedicated to the vacuum gas oil cut.

According to one form of this embodiment, the middle distillate cut and/or the vacuum gas oil
 25 cut can be sent to a dedicated hydrotreating section which is different from the section for hydrotreating the naphtha cut of step d). In this case, the operating conditions, in particular the temperature and the pressure, can be higher than those of the step of hydrotreating the naphtha cut in order to remove the sulfur- and nitrogen-based impurities, which are often greater and more refractory in this cut.

30 In this case, at least a portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut can be subjected to a dedicated hydrotreating step, in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with said heavy cut, or said middle distillate

cut and/or said vacuum gas oil cut and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an average temperature between 250°C and 430°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrotreated heavy effluent.

5

According to another form of this embodiment, the middle distillate cut and/or the vacuum gas oil cut can be reintroduced into the process according to the invention by introducing said middle distillate cut or said vacuum gas oil cut into the hydrogenation step c) and/or into hydrotreating step d). Specifically, the middle distillate cut or the vacuum gas oil cut contains

10 few diolefins (which are found after the prefractionation mainly in the naphtha cut) and can therefore by-pass the selective hydrogenation step b), thus making it possible to use a selective hydrogenation section which is smaller in size.

In this case, the separation step e) may comprise fractionation, for example by distillation, into at least one naphtha cut and one middle distillate cut and/or a vacuum gas oil cut which

15 are stripped of their impurities.

The middle distillate cut stripped of its impurities can subsequently be introduced, alone or as a mixture with the naphtha cut stripped of its impurities, into a steam cracking unit or be sent to a fuel storage unit, for example a unit for the storage of diesel or a unit for the storage of kerosene, resulting from conventional petroleum feedstocks, or else be recycled to a step of

20 the process according to the invention, for example to steps c) and/or d).

The vacuum gas oil cut stripped of its impurities can subsequently be introduced, alone or as a mixture with the middle distillate cut, into a hydrocracking unit or into a fluid catalytic cracking unit or else be recycled to a step of the process according to the invention, for example to steps c) and/or d).

25 **Hydrocracking**

The hydrotreated heavy effluent (the hydrotreated heavy cut, or the hydrotreated middle distillate cut and/or the hydrotreated vacuum gas oil cut) resulting from the heavy cut during the prefractionation step a) can subsequently be introduced into a hydrocracking step which makes it possible to convert the cut into lighter and more upgradable products (naphtha,

30 middle distillate). The compounds having a boiling point above 175°C contain, relative to lighter compounds, more naphthenic, naphthenic-aromatic and aromatic compounds, thus leading to a higher C/H ratio. This high ratio is a cause of coking in the steam cracker, thus requiring steam cracking furnaces dedicated to this cut. When it is desired to minimize the yield of these heavy compounds (middle distillates cut) and to maximize the yield of light

35 compounds (naphtha cut), these compounds can be at least partly converted into light compounds by hydrocracking, a cut generally favoured for a steam cracking unit.

It is also possible to carry out a co-processing by mixing the hydrotreated heavy cut or the hydrotreated middle distillate cut and/or the hydrotreated vacuum gas oil cut with a petroleum feedstock and/or a feedstock resulting from the conversion of biomass. Such a feedstock is generally a hydrocarbon feedstock, at least 50% by weight of the compounds of which have an initial boiling point above 300°C and a final boiling point below 650°C. It can be chosen from HCOs (Heavy Cycle Oil (heavy gas oils resulting from a catalytic cracking unit)), vacuum distillates, for example gas oils resulting from the direct distillation of crude oil or from conversion units, such as catalytic cracking units, cokers or visbreaking units, feedstocks originating from units for the extraction of aromatics, lubricating oil bases or resulting from the solvent dewaxing of lubricating oil bases, distillates originating from processes for the fixed-bed or ebullated-bed desulfurization or hydroconversion of atmospheric residues and/or vacuum residues and/or deasphalted oils, or else the feedstock can be a deasphalted oil or comprise vegetable oils or else originate from the conversion of feedstocks resulting from biomass. It can also be paraffins resulting from the Fischer-Tropsch process. Said feedstock can also be a mixture of said abovementioned feedstocks. Preferably, when it is desired to carry out a co-processing, the co-feedstock is a vacuum distillate.

The hydrocracking is carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrocracking catalyst, said hydrocracking reaction section being fed with said hydrotreated heavy effluent (the hydrotreated heavy cut, or the hydrotreated middle distillate cut and/or the hydrotreated vacuum gas oil cut) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed at an average temperature between 250°C and 480°C, a hydrogen partial pressure between 1.5 and 20.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrocracked effluent.

Thus, said hydrocracking reaction section is advantageously implemented at an average temperature of between 250 and 480°C, preferably between 320 and 450°C, at a hydrogen partial pressure of between 1.5 and 20.0 MPa abs., preferably between 2 and 18.0 MPa abs., and at an hourly space velocity (HSV) of between 0.1 and 10.0 h⁻¹, preferably between 0.1 and 5.0 h⁻¹, preferentially between 0.2 and 4 h⁻¹. The hydrogen coverage in the hydrocracking step is advantageously between 80 and 2000 Nm³ of hydrogen per m³ of feedstock which feeds the hydrocracking step, and preferably between 200 and 1800 Nm³ of hydrogen per m³ of feedstock which feeds the hydrocracking step. The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above.

The hydrotreatment step and the hydrocracking step can advantageously be carried out in the same reactor or in different reactors. When they are carried out in the same reactor, the reactor comprises several catalyst beds, the first catalyst beds comprising the hydrotreatment catalyst(s) and the following catalyst beds comprising the hydrocracking catalyst(s).

The hydrocracking step can be carried out in one or two steps. When it is carried out in two steps, a separation of the effluent from the first hydrocracking step is carried out, making it possible to obtain a heavy cut (middle distillate cut and/or unreacted vacuum gas oil cut), which is introduced into the second hydrocracking step comprising a second dedicated hydrocracking reaction section, different from the first hydrocracking reaction section. This configuration is particularly suitable when it is desired to produce only a naphtha cut. The preferred operating conditions and the catalysts used in the second hydrocracking step are those described for the first hydrocracking step. The operating conditions and catalysts used in the two hydrocracking steps can be identical or different.

The hydrocracking catalyst(s) used in the hydrocracking step(s) are conventional hydrocracking catalysts known to a person skilled in the art, of bifunctional type combining an acid function with a hydrogenating-dehydrogenating function and optionally at least one binding matrix. The acid function is contributed by supports of high surface area (generally 150 to 800 m²/g) exhibiting a surface acidity, such as halogenated (in particular chlorinated or fluorinated) aluminas, combinations of boron and aluminium oxides, amorphous silica-aluminas and zeolites. The hydrogenating-dehydrogenating function is contributed by at least one metal from group VIB of the Periodic Table and/or at least one metal from group VIII. Hydrogenating-dehydrogenating functions of NiMo, NiMoW or NiW type are preferred.

The contents of metals are generally as described for the hydrotreating catalysts.

The hydrocracking catalysts can also contain phosphorus and/or an organic compound containing oxygen and/or nitrogen and/or sulfur in contents as described for the hydrotreating catalysts.

The hydrocracked effluent is subsequently generally subjected to a fractionation step which makes it possible to recover lighter cuts, for example a naphtha cut and at least one middle distillate cut, and an unconverted cut which can be recycled to the hydrocracking step. The naphtha cut and/or at least one middle distillate cut can subsequently be sent to a steam cracking unit or be sent to a fuel storage unit or else be recycled to a step of the process according to the invention, for example to steps c) and/or d).

FCC

The heavy cut, or the middle distillate cut and/or the vacuum gas oil cut resulting from the heavy cut during the prefractionation step a), which is optionally hydrotreated, can also be subjected to a fluid catalytic cracking (FCC) step in order to produce products such as petrol having a high octane number, a light fuel oil, a heavy fuel oil, a light gas rich in olefins (propylene, butylene) and coke.

It is also possible to carry out a co-processing by mixing the heavy cut, or the middle distillate cut and/or the vacuum gas oil cut, which is optionally hydrotreated, with a petroleum feedstock and/or a feedstock resulting from the conversion of biomass. Such a feedstock is an atmospheric gas oil, a vacuum gas oil and an atmospheric residue, a lignocellulosic feedstock or more generally a feedstock resulting from biomass, which are taken alone or as a mixture.

The FCC unit uses a high-activity zeolite catalyst to crack heavy hydrocarbon molecules. A conventional FCC unit is used. For example, a summary description of catalytic cracking (the first industrial use of which goes back to 1936 (Houdry process) or to 1942 for the use of a fluidized bed catalyst) will be found in Ullmann's Encyclopedia of Industrial Chemistry, Volume A 18, 1991, pages 61 to 64. The choice of the catalyst and of the operating conditions depends on the products desired as a function of the feedstock treated, as is, for example, described in the paper by M. Marcilly, pages 990-991, published in the revue de l'institut français du pétrole [Review of the French Institute of Petroleum], Nov.-Dec. 1975, pages 969-1006.

Fluid catalytic cracking is generally carried out in a fluid catalytic cracking reaction section in a substantially vertical reactor, either in upflow (riser) mode or in downflow (downer) mode, in the presence of the heavy cut or of the middle distillate cut and/or of the vacuum gas oil cut and of a zeolite catalyst at a reactor temperature of between 450°C and 600°C with a contact time in the reactor of less than 1 minute, often of 0.1 to 50 seconds.

A conventional zeolite catalyst comprising a matrix, optionally an additive and at least one zeolite is typically used in the FCC process. The amount of zeolite is variable but is usually from 3% to 60% by weight, often from 6% to 50% by weight, and most often from 10% to 45% by weight, relative to the weight of the catalyst. The zeolite is usually dispersed in the matrix. The amount of additive is usually from 0% to 30% by weight and often from 0% to 20% by weight, relative to the weight of the catalyst. The amount of matrix represents the balance to 100% by weight. The additive is generally chosen from the group formed by the oxides of metals from Group IIa of the Periodic Table of the Elements, such as, for example, magnesium oxide or calcium oxide, rare-earth metal oxides and titanates of metals from Group IIa. The matrix is generally a silica, an alumina, a silica-alumina, a silica-magnesia, a

clay or a mixture of two or more of these products. The most commonly used zeolite is zeolite Y.

Heavy metal adsorption step (optional)

Any gaseous effluent and/or any liquid effluent obtained from the separation step e) may be subjected to an optional heavy metal adsorption step.

The optional adsorption step makes it possible to remove or reduce the amount of metal impurities, in particular the amount of heavy metals, such as arsenic, zinc, lead and in particular mercury, possibly present in said gaseous and liquid effluents. The metal impurities, and in particular the heavy metals, are present in the feedstock. Some impurities, in particular based on mercury, can be transformed in one of the steps of the process according to the invention. Their transformed form is easier to trap. Their elimination or reduction may in particular be necessary when a portion of at least of said gaseous and liquid effluents is intended to be sent, either directly or after having been subjected to one or more optional additional separation steps, to a step having strict specifications for metal impurities, such as a steam cracking step.

Thus, an optional step of adsorption of a gaseous effluent and/or of a hydrocarbon effluent resulting from the process according to the invention is advantageously carried out in particular when at least one of these effluents or the feedstock respectively comprise more than 20 ppb by weight, in particular more than 15 ppb by weight, of metal elements of heavy metals (As, Zn, Pb, Hg, and the like), and in particular when at least one of these effluents or the feedstock respectively comprise more than 10 ppb by weight of mercury, more particularly more than 15 ppb by weight of mercury.

Said optional adsorption step is advantageously carried out at a temperature between 20°C and 250°C, preferably between 40°C and 200°C, and at a pressure between 0.15 and 10.0 MPa abs., preferably between 0.2 and 1.0 MPa abs.

Said optional adsorption step can be carried out by any adsorbent known to a person skilled in the art which makes it possible to reduce the amount of such contaminants.

According to a variant, said optional adsorption step is carried out in an adsorption section operated in the presence of at least one adsorbant comprising a porous support, and optionally at least one active phase which may be based on sulfur in the elemental form, or in the metal sulfide or metal oxide form, or else in the metal form in elemental form.

The porous support can be chosen without distinction from the families of the aluminas, silicas-aluminas, silicas, zeolites and/or activated carbons. Advantageously, the porous support is based on alumina.

Said adsorption section can comprise one or more adsorption columns. When the adsorption section comprises two adsorption columns, one operating mode can be a “swing” operation, in which one of the columns is on-line, that is to say in operation, while the other column is in reserve. Another operating mode is to have at least two columns operating in series in permutable mode.

Preferably, said adsorption section comprises an adsorption column for the gaseous effluent(s) and an adsorption column for the liquid effluent(s).

Analysis methods used

The analysis methods and/or standards used to determine the characteristics of the various streams, in particular of the feedstock to be treated and of the effluents, are known to those skilled in the art. They are in particular listed below in Table 1 by way of information. Other methods reputed to be equivalent can also be used, in particular equivalent IP, EN or ISO methods:

Table 1

Description	Methods
Density @ 15°C	ASTM D4052
Sulfur Content	ISO 20846
Nitrogen Content	ASTM D4629
Acid Number	ASTM D664
Bromine Number	ASTM D1159
Maleic Anhydride Value (MAV)	MAV method (1)
Content of Oxygen-Containing Molecules	Combustion + Infrared
Content of Paraffins	UOP990-11
Content of Naphthenes and Olefins	UOP990-11
Content of Aromatics	UOP990-11
Content of Halogens	ASTM D7359
Chlorine content	ASTM D7536
Content of Metals:	ASTM D5185
P	
Fe	

Si	
Na	
B	
Simulated distillation	ASTM D2887

(1) MAV method described in the paper: 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, pp. 57-68

LIST OF FIGURES

- 5 The particulars of the elements referenced in Figures 1 to 2 enables a better understanding of the invention, without the latter being limited to the specific embodiments illustrated in Figures 1 and 2. The various embodiments presented can be used alone or in combination with one another, without limitation of combination.

10 Figure 1 represents the diagram of a specific embodiment of the process of the present invention, comprising:

- a step a) of prefractionation of a feedstock comprising a plastic and/or tyre and/or solid recovered fuel pyrolysis oil 1 in order to obtain a naphtha cut 2, a middle distillate cut 3 and a vacuum gas oil (VGO) cut 4;
- a selective hydrogenation step b) carried out in a reaction section fed with said naphtha cut 2 and a gas stream comprising hydrogen 5, in the presence of at least one selective hydrogenation catalyst, and optionally of an amine contributed by the stream 6 and optionally of a sulfur compound contributed by the stream 7, in order to obtain a selectively hydrogenated effluent 8;
- 15 - a step c) of hydrogenating the selectively hydrogenated effluent 8 resulting from step b), in the presence of hydrogen 9, carried out in at least one fixed-bed reactor comprising at least one hydrogenation catalyst, in order to obtain a hydrogenated effluent 10;
- a step d) of hydrotreating the hydrogenated effluent 10 resulting from step b), in the presence of hydrogen 11, carried out in at least one fixed-bed reactor comprising at least one hydrotreating catalyst, in order to obtain a hydrotreated effluent 12;
- 20 - a separation step e), fed with the hydrotreated effluent 12 obtained from step d) and an aqueous solution 13, said step being performed at a temperature of between 20°C and 300°C, in order to obtain at least a gaseous effluent 14, an aqueous effluent 15 and a naphtha cut stripped of its impurities 16.

On conclusion of step e), a portion of the naphtha cut stripped of its impurities 16 can be sent to a steam cracking process (not represented). Another portion of the naphtha cut stripped of its impurities 16 can feed the hydrogenation step c) and/or the hydrotreating step d) as recycle (not represented).

- 5 The middle distillate cut 3 can be sent to a dedicated hydrotreating stage, be subjected to a stripping in order to remove in particular the hydrogen and the H_2S , and then be sent to a fuel storage unit, for example a unit for storing diesel or a unit for storing kerosene, resulting from conventional petroleum feedstocks (not represented).

- 10 The vacuum gas oil (VGO) cut 4, and optionally the middle distillate cut, can be introduced into a dedicated hydrotreating step, then into a hydrocracking step, be subjected to a separation step in order to remove in particular the hydrogen and the H_2S and a heavy cut which has not been hydrocracked, then be sent to a fuel storage unit, for example a unit for storing diesel or a unit for storing kerosene, originating from conventional petroleum feedstocks (not represented).

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- Figure 2 represents the diagram of a specific embodiment of the process of the present invention which is based on the diagram of Figure 1. The middle distillate cut 3 and/or the vacuum gas oil (VGO) cut 4 can be reintroduced into the process according to the invention, in particular in steps c) and/or d). In this case, the separation step e) includes a fractionation step making it possible to obtain said naphtha cut 16 and a hydrotreated heavier cut 17. The hydrotreated heavier cut 17 can be introduced into a hydrocracking step or into a fluid catalytic cracking step (not shown).

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- Only the main steps, with the main streams, are represented in Figures 1 and 2, in order to enable the invention to be better understood. It is clearly understood that all the items of equipment required for the operation are present (drums, pumps, exchangers, furnaces, columns, and the like), even if they are not represented. It is also understood that hydrogen-rich gas streams (makeup or recycle streams), as described above, can be injected at the inlet of each reactor or catalyst bed or between two reactors or two catalyst beds. Means well known to a person skilled in the art for the purification and recycling of hydrogen can also be employed.

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EXAMPLE

The feedstock 1 treated in the process is a plastic pyrolysis oil (that is to say, comprising 100% by weight of said plastic pyrolysis oil).

The feedstock 1 is subjected to a prefractionation step a) in order to obtain a naphtha cut 2 having a boiling point between 36°C and 180°C and a heavy cut (180°C+ distillates) having a boiling point of above 180°C. The characteristics of the feedstock and of the cuts are shown in Table 2.

By virtue of the fractionation, certain impurities which are particularly harmful to the steam cracking unit end up more concentrated in the light naphtha fraction. This concerns the chlorine compounds, silicon compounds, monoolefins and diolefins.

Conversely, these same compounds are less concentrated in the heavier 180°C+ fraction, which promotes their treatment in downstream units directly in co-processing. In particular, the content of chlorine compounds/silicon compounds obtained within the heavy cut (Cl = 30 ppm by weight, Si = 15 ppm by weight) after prefractionation enables this fraction to be incorporated directly in the feedstock of the FCC unit.

Table 2: Characteristics of the feedstock and of the cuts after prefractionation

Property	Method	Unit	Feedstock	Naphtha Cut IBP-180°C	Distillate Cut – 180°C+
Prefractionation Yield (% w/w)		% w/w		24.6	75.4
Density at 15°C	NF EN ISO 12185	g/cm ³	0.798	0.750	0.817
Bromine Number	ASTM D1159	g/100 g	51.5	84.6	36
MAV	IFPEN 9407	mg/g	10.8	18.2	7.7
S	ASTM D5453	mg/kg	67	71	71
N	ASTM D4629	mg/kg	871	526	982
Cl	ASTM D7536	mg/kg	95	247	30
Si	ASTM D5185	mg/kg	20	33	15
Simulated Distillation	ASTM D2887				
Initial boiling point (0.50%)		°C	60	59	167
10%		°C	134	81	193
30%		°C	199	123	249
50%		°C	270	148	303
70%		°C	335	166	351
90%		°C	403	182	423
Final boiling point (99.50%)		°C	574	195	573

The naphtha cut 2 is subjected to a selective hydrogenation step b) carried out in a fixed-bed reactor and in the presence of hydrogen 5 and of a selective hydrogenation catalyst of NiMo on alumina type, under the conditions indicated in Table 3.

Table 3: conditions of the selective hydrogenation step b)

Average selective hydrogenation temperature (WABT)	°C	180
Hydrogen partial pressure at the outlet of the reactor	MPa abs	5.75
H ₂ /HC at the inlet of the reactor (hydrogen coverage by volume, relative to the volume of feedstock)	Nm ³ /m ³	20
HSV (volume flow rate of feedstock/volume of catalysts)	h ⁻¹	2
Number of beds	-	1
Reaction exotherm, i.e. ΔT of the reactor	°C	< 25°C

On conclusion of the selective hydrogenation step b), all of the diolefins initially present in the feedstock were converted along with a very slight fraction of the monoolefins (<5% by weight). Given the high exothermicity of the reactions involved, the concentration of the olefins/diolefins within the naphtha feedstock presents a challenge in terms of controlling the thermal profile.

According to Table 3, the temperature difference between the inlet and the outlet of the reactor is reasonable ($\Delta T < 25^\circ\text{C}$) under the chosen operating conditions.

The selectively hydrogenated effluent 8 obtained from the selective hydrogenation step b) is subjected directly, without separation, to a hydrogenation step c) carried out in a fixed bed and in the presence of hydrogen 9, and of a hydrogenation catalyst of NiMo on alumina type under the conditions presented in Table 4.

Table 4: Conditions of the hydrogenation step c)

Average hydrogenation temperature (WABT)	°C	280
H ₂ /HC at the inlet of the reactor (hydrogen coverage by volume relative to the total feedstock volume) (3)	Nm ³ /m ³	200
HSV (volume flow rate of feedstock/volume of catalysts)	h ⁻¹	0.5

(3) Defined here with respect to the volume of total liquid feedstock under standard conditions, i.e. fresh feedstock + liquid recycle/quench if applicable

On conclusion of the hydrogenation step c), all of the olefins initially present in the feedstock were converted. Given the high exothermicity of the reactions involved, the concentration of these compounds within the naphtha feedstock presents a challenge in terms of controlling the thermal profile. The exotherm of this reaction section is controlled either by injection of a gas stream (option 1 – gaseous quench) or by injection of a liquid stream, notably the recycled hydrotreated naphtha cut (option 2 – liquid quench) (Table 5).

Configurations intermediate between these 2 options in terms of number of beds, recycling ratio, nature of the quench (gas and/or liquid) are possible in order to control the reaction exotherm.

Table 5: Control of the exotherm of the hydrogenation step c)

	Option 1 – gas quench	Option 2 – liquid quench
Implementation of the process	- <u>Nature of the quench</u>: H₂-rich gas from the separation step e) - <u>Injection point(s)</u>: gas quench between each bed	- <u>Nature of the quench</u>: hydrotreated liquid effluent from the separation step e) - <u>Injection point(s)</u>: upstream of bed 1 (as dilution with the feedstock) and an injection between beds 1 and 2
Number of beds	6	2
Recycle ratio	<u>H₂ coverage at bed inlet</u> : - Bed 1: 200 NI/l at inlet - Bed 6: 1200 NI/l at inlet	<u>Amount of recycled liquid effluent</u> : - in bed 1: weight ratio between the recycled liquid fraction and naphtha feedstock = 1 - between beds 1 and 2: weight ratio between the recycled liquid effluent flow rate and naphtha feedstock = 0.35
Minimum ppH₂ within step c)	3.5 MPa at the outlet of bed 1	3.5 MPa at the outlet of bed 2
Exotherm, i.e. ΔT per bed	< 25°C	< 25°C

The hydrogenated effluent 10 resulting from the hydrogenation step c) is subjected directly, without separation, to a hydrotreating step d) carried out in a fixed bed and in the presence of hydrogen 11 and of a hydrotreating catalyst of NiMo-on-alumina type under the conditions presented in Table 6. A fraction of the hydrogen-rich gas resulting from the separation step e) is mixed with the hydrogenated effluent resulting from step c) in order to satisfy the criteria of average temperature (WABT) and H₂/HC ratio of the hydrotreating step d).

Table 6: conditions of the hydrotreating step d)

		Option 1 – gas quench	Option 2 – liquid quench
Hydrotreating average temperature (WABT)	°C	280	280
Hydrogen partial pressure at the outlet of the reactor	MPa abs	5.2	3.5
H ₂ /HC (hydrogen coverage by volume, relative to the volume of feedstock) (3)	Nm ³ /m ³	1300	250
HSV (volume flow rate of feedstock/volume of catalysts)	h ⁻¹	0.5	0.5
Number of beds	-	1	1
Exotherm, i.e. ΔT per bed	°C	< 5	< 5

(3) Defined here with respect to the volume of total liquid feedstock under standard conditions, i.e. fresh feedstock + liquid recycle/quench if applicable

On conclusion of the hydrotreating step c), the sulfur and nitrogen compounds and also the aromatics are sufficiently converted to meet the specifications for entry into the steam cracker (Table 8). From a reaction exotherm viewpoint, it should be noted that:

- on the one hand, the reconcentration phenomenon observed for the olefins/diolefins within the naphtha cut is not valid for the sulfur, nitrogen and aromatic compounds,
- the exotherm of the reactions for hydrodenitrogenation, hydrodesulfurization and hydrogenation of the aromatics is lower than for the hydrogenation of the olefins.

Thus, according to Table 6, the temperature difference between the inlet and the outlet of the hydrotreating reactor does not pose a challenge ($\Delta T < 5^\circ\text{C}$) in the process according to the invention.

The hydrotreated effluent 12 resulting from the hydrotreating step d) is subjected to a separation step e) in which a stream of water is injected into the effluent resulting from the hydrotreating step d); the mixture having reached a temperature of 45°C , it is subsequently separated in a knockout drum so as to obtain a hydrogen-rich gaseous effluent sent to a column for washing the acid gases, and a liquid effluent which is subsequently treated in a two-phase knockout drum so as to obtain an aqueous effluent and a washed naphtha cut.

The washed naphtha fraction is then sent to a stripping column so as to obtain a naphtha fraction stripped of its impurities. The naphtha cut can also, according to option 2) of Tables 5 and 6, be recycled to the hydrogenation step c) so as to control the reaction exotherms.

The yields and qualities obtained after separation are shown in Table 7 (the yields corresponding to the ratios of the amounts by weight of the various products obtained, with respect to the weight of feedstock upstream of step b), expressed as percentage and denoted % w/w). The various options 1 and 2 furthermore have no effect on yields and quality of the products.

Table 7: Yields of the various products obtained after separation and fractionation

NH ₃ + H ₂ S	% w/w	0.1
C ₁ -C ₄	% w/w	0.3
IBP+ Naphtha liquid cut after stripping	% w/w	100.4

The characteristics of the IBP+ liquid naphtha cut obtained after the separation step e) are presented in Table 8.

Table 8: Characteristics of the IBP+ liquid naphtha fraction

Property	Method	Unit	IBP+ Naphtha Cut
Density at 15°C	NF EN ISO 12185	g/cm ³	0.740
Bromine Number	ASTM D1159	g/100 g	< 0.8
S	ASTM D5453	mg/kg	2
N	ASTM D4629	mg/kg	< 5
Cl	ASTM D7536	ppb by weight	Not detected
Si	ASTM D5185	mg/kg	< 0.2
Fe	ASTM D5185	mg/kg	Not detected
Total Metals	ASTM D5185	mg/kg	Not detected
Simulated Distillation	ASTM D2887		
Initial boiling point (0.50%)		°C	52
10%		°C	75
30%		°C	118
50%		°C	144
70%		°C	163
90%		°C	180
Final boiling point (99.50%)		°C	194

The IBP+ naphtha cut has a composition compatible with a steam cracking unit, since:

- it contains no diolefins and little in the way of monoolefins;
- it has a content of chlorine element which is very low (content not detected) and lower than the limit required for a steam cracker feedstock (≤ 50 ppb by weight);
- it has contents of metals, in particular of iron (Fe) and of silicon, which are very low (content of metals not detected; content of Fe not detected; content of Si < 0.2 ppm by weight) and lower than the limits required for a steam cracker feedstock (≤ 5.0 ppm by weight, very

preferably ≤ 1 ppm by weight, for the metals; ≤ 100 ppb by weight for Fe; ≤ 0.6 ppm by weight for Si);

- finally, it contains little sulfur (2 ppm by weight) and little nitrogen (< 5 ppm by weight), these contents being far below the limits required for a steam cracker feedstock (≤ 500 ppm by

5 weight, preferably ≤ 200 ppm by weight, for S and N).

CLAIMS

1. Process for treating a feedstock comprising a plastic and/or tyre and/or solid recovered fuel pyrolysis oil, said process comprising the following steps:

- a) a step of prefractionating the feedstock in order to obtain a naphtha cut and at least one heavier cut,
- b) a selective hydrogenation step carried out in a reaction section fed with said naphtha cut and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature of between 100°C and 260°C, a hydrogen partial pressure of between 1.0 and 10.0 MPa abs. and an hourly space velocity of between 0.1 and 10.0 h⁻¹, in order to obtain a selectively hydrogenated effluent,
- c) a hydrogenation step carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrogenation catalyst, said hydrogenation reaction section being fed at least with said selectively hydrogenated effluent obtained from step b) and a gas stream comprising hydrogen, said hydrogenation reaction section being employed at an average temperature between 180°C and 380°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrogenated effluent,
- d) optionally, a hydrotreating step carried out in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with said hydrogenated effluent obtained from step c) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an average temperature between 200°C and 400°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrotreated effluent;
- e) a separation step, fed with the hydrogenated effluent obtained from step c) or with the hydrotreated effluent obtained from step d) and an aqueous solution, said step being carried out in a separation section at a temperature between 20°C and 300°C, in order to obtain at least a gaseous effluent, an aqueous effluent and a naphtha cut stripped of its impurities.

2. Process according to Claim 1, comprising the hydrotreating step d).

3. Process according to either of the preceding claims, in which the naphtha cut obtained in step e) is at least partly sent to a steam cracking unit.

4. Process according to the preceding claim, in which the steam cracking is carried out in at least one pyrolysis furnace at a temperature of between 700°C and 900°C and at a pressure of between 0.05 and 0.3 MPa relative in the presence of steam.
5. Process according to one of the preceding claims, in which a liquid and/or gaseous diluent is injected in step b), c) and/or d).
6. Process according to the preceding claim, in which the liquid diluent is a portion of the naphtha cut obtained in step e) and the gaseous diluent is the gaseous effluent obtained in step e).
7. Process according to one of the preceding claims, comprising at least one step of pretreating the feedstock or the naphtha cut obtained in step a), said pretreatment step being carried out before or after the prefractionation step a) and upstream of the selective hydrogenation step b) and comprising an adsorption step and/or a filtration step and/or a centrifugation step and/or a decantation step and/or an electrostatic separation step and/or a step of washing with an aqueous solution and/or a gas stripping step.
8. Process according to one of the preceding claims, in which said selective hydrogenation catalyst of step b) comprises a support chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising at least one group VIII element and/or at least one group VIB element.
9. Process according to one of the preceding claims, in which said hydrogenation catalyst of step c) comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising either at least one group VIII element and at least one group VIB element, or at least one group VIII element.
10. Process according to one of the preceding claims, in which said hydrotreating catalyst of step d) comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and mixtures thereof, and a hydrogenating-dehydrogenating function comprising at least one group VIII element and/or at least one group VIB element.
11. Process according to one of the preceding claims, in which the feedstock consists of a plastic and/or tyre and/or solid recovered fuel pyrolysis oil.

12. Process according to any one of the preceding claims, in which said prefractionation step a) is carried out so as to obtain said naphtha cut and at least one middle distillate cut and a vacuum gas oil cut.

13. Process according to one of the preceding claims, in which at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut is reintroduced in step c) and/or d).

14. Process according to any one of the preceding claims, in which at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut is subjected to a dedicated hydrotreating step, in a hydrotreating reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with said heavy cut, or said middle distillate cut and/or said vacuum gas oil cut and a gas stream comprising hydrogen, said hydrotreating reaction section being employed at an average temperature between 250°C and 430°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrotreated heavy effluent.

15. Process according to the preceding claim, in which at least one portion of the hydrotreated heavy effluent is sent to a hydrocracking step carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalyst beds, n being an integer greater than or equal to 1, each comprising at least one hydrocracking catalyst, said hydrocracking reaction section being fed at least with said hydrotreated heavy effluent and a gas stream comprising hydrogen, said hydrocracking reaction section being employed at an average temperature between 250°C and 480°C, a hydrogen partial pressure between 1.5 and 20.0 MPa abs. and an hourly space velocity between 0.1 and 10.0 h⁻¹, in order to obtain a hydrocracked effluent.

16. Process according to Claims 1 to 14, in which at least one portion of said heavy cut, or of said middle distillate cut and/or of said vacuum gas oil cut, or of the hydrotreated heavy effluent is sent to a fluid catalytic cracking step carried out in a fluid catalytic cracking reaction section in a substantially vertical reactor, either in riser mode or in downer mode, in the presence of a zeolite catalyst at a reactor temperature of between 450°C and 600°C with a contact time in the reactor of less than 1 minute.

17. Product obtained by the process according to one of Claims 1 to 16.

18. Product according to Claim 17, comprising a content of biological carbon according to ASTM D6866 of between 0% and 70% by weight.