

METHOD FOR TREATING A TYRE PYROLYSIS OIL

TECHNICAL FIELD

The present invention falls within the field of the recycling of tyres. More particularly, the present invention relates to a process for treating a feedstock comprising a pyrolysis oil of which at least 5% by weight of the pyrolysis oil is derived from tyres. Tyre pyrolysis oils generally contain a considerable content of sulfur. The process makes it possible to at least partly remove impurities that said feedstock may contain in relatively large amounts, while at the same time reducing, by the use of a pyrolysis oil with a high loading of sulfur compounds, the consumption of sulfiding agent to be added in order to maintain the catalysts in sulfide form in the catalytic steps of the process.

PRIOR ART

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

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

However, pyrolysis oils have impurities at often high contents which are 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 of corrosion (in particular due to the presence of chlorine), of coking or of catalytic deactivation, or also 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 which may be present in the pyrolysis oil can give rise to problems of clogging in the processes.

One way of removing these impurities contained in the pyrolysis oils is to carry out a hydrotreatment (HDT) in the presence of catalysts. Such processes are, for example, described in WO2018/055555, WO2021/165178 or also WO2022/144235.

The patent application WO2022/144235 describes a process for the treatment of a plastics pyrolysis oil targeted at reducing and/or at removing the impurities contained in the pyrolysis oil in order to obtain an effluent compatible for a steam cracker. The process comprises the following steps:

- a) the hydrogenation of said feedstock in the presence at least of hydrogen and of at least one hydrogenation catalyst at an average temperature of between 140 and 340°C, the outlet temperature of step a) being at least 15°C greater than the inlet temperature of step a), in order to obtain a hydrogenated effluent;
- b) the hydrotreatment of said hydrogenated effluent in the presence at least of hydrogen and of at least one hydrotreatment catalyst, in order to obtain a hydrotreated effluent, the average temperature of step b) being greater than the average temperature of step a);
- c) a separation of the hydrotreated effluent in the presence of an aqueous stream, at a temperature of between 50 and 370°C, in order to obtain at least one gaseous effluent, an aqueous liquid effluent and a hydrocarbon liquid effluent.

One route for removing the impurities contained in the pyrolysis oils is thus to carry out a hydrotreatment in the presence of catalysts which are active in sulfide form.

In the context of feedstocks containing a plastics pyrolysis oil, the feedstocks available are generally fairly poor in sulfur. However, a minimum H_2S_{pp} is necessary in the hydrotreatment reactor in order to maintain the catalysts in sulfide form and thus not to reduce them. In order to maintain a sufficient H_2S_{pp} in the reactor and in view of the fact that the ex-plastic feedstocks do not contain sufficient sulfur, a sulfiding agent is generally, indeed even necessarily, continuously added, typically DMDS (dimethyl disulfide), to the feedstock. The sulfiding agent decomposes very rapidly to give H_2S by the action of the temperature and of the hydrogen at the reactor inlet and thus provides the amount of H_2S necessary to ensure a minimum and sufficient H_2S_{pp} .

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

The process according to the invention takes advantage in particular of the considerable amount of sulfur impurities contained in a tyre pyrolysis oil by using the sulfur impurities as sulfiding agent in order to maintain the catalysts in sulfide form in the catalytic steps of the process. The act of using a tyre pyrolysis oil thus makes it possible to greatly minimize the consumption of sulfiding agent that conventionally is to be added, generally of DMS type.

SUMMARY OF THE INVENTION

More precisely, the invention relates to a process for treating a feedstock comprising at least 5% by weight of a tyre pyrolysis oil relative to the total weight of the feedstock, said tyre pyrolysis oil having a sulfur content of between 2000 and 10 000 ppm by weight relative to the total weight of the tyre pyrolysis oil, said process comprising the following steps:

a) optionally a selective hydrogenation step carried out in a reaction section employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one selective hydrogenation catalyst, said selective hydrogenation reaction section being fed at least with said feedstock and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature between 100 and 280°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 selectively hydrogenated effluent,

b) a hydrogenation step carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalytic 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 feedstock or said selectively hydrogenated effluent obtained from step a) and a gas stream comprising hydrogen, said hydrogenation reaction section being implemented at an average temperature between 140 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 hydrogenated effluent,

c) a hydrotreatment step carried out in a hydrotreatment reaction section, employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment reaction section being fed at least with said hydrocarbon effluent obtained from step d) when separation step d) is carried out between steps b) and c), and/or at least with the hydrogenated effluent obtained from step b) when separation step d) is carried out after step c), and a gas stream comprising hydrogen, said hydrotreatment reaction section being implemented at an average

temperature between 250 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 effluent,

d) a separation step, carried out between steps b) and c) and/or after step c), said step being fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c) when separation step d) is carried out after step c), and an aqueous solution, said step being performed in a separation section, in order to obtain at least one gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

The present invention thus relates to a process making it possible to purify an oil resulting from the pyrolysis of tyres, optionally supplemented with pyrolysis oil obtained from plastics and/or SRFs, of at least part of its impurities, which makes it possible to hydrogenate it and thus to be able to upgrade it in particular by incorporating it directly in the fuel storage unit or else by rendering it compatible with a treatment in a steam cracking unit while being able to considerably reduce the consumption of sulfiding agent.

Another advantage of the invention is that of preventing risks of plugging and/or corrosion of the treatment unit in which the process of the invention is performed, the risks being exacerbated by the presence, often in large amounts, of diolefins, metals and halogen compounds in a pyrolysis oil. 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 the ammonium chloride salts which form by reaction between the chloride ions, released by the hydrogenation of the chlorine compounds in HCl form in particular during the hydrogenation step followed by dissolution in water, and the ammonium ions, generated by the hydrogenation of the nitrogen compounds in the form of NH₃ during the hydrotreatment step and/or supplied by injection of an amine when the content of chlorine compounds is high, followed by dissolution in water. The high content of nitrogen compounds in a tyre pyrolysis oil makes it possible to lower or even eliminate the need to add a nitrogen compound, which is another advantage of the invention.

The process of the invention thus makes it possible to obtain a hydrocarbon effluent resulting from a tyre pyrolysis oil which is at least partly freed of the impurities of the starting tyre pyrolysis oil, thus limiting the problems of operability, such as the problems of corrosion, of coking or of catalytic deactivation, to which these impurities may give rise, in particular in steam cracking units and/or in units located downstream of the steam cracking units.

According to a variant, the feedstock comprises a plastics and/or solid recovered fuels pyrolysis oil.

According to a variant, the feedstock consists of a tyre pyrolysis oil and of plastics and/or solid recovered fuels pyrolysis oil(s).

According to a variant, the feedstock comprises a tyre pyrolysis oil in a content of between 5% and 99% by weight and a plastics and/or SRF pyrolysis oil in a content of between 1% and 95% by weight relative to the total weight of the feedstock.

According to a variant, separation step d) comprises the following steps:

d1) a separation step, fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c) when separation step d) is carried out after step c), said step being performed at a temperature greater than the precipitation temperature of the ammonium halides and at a pressure substantially identical to the pressure of step b) in order to obtain at least one first gaseous effluent and a liquid effluent of which a part is optionally recycled, as recycled effluent, upstream of step b),

d2) a separation step, fed with the first gaseous effluent and optionally at least a part of the liquid effluent obtained from step d1), and an aqueous solution, said step being performed at a temperature lower than the precipitation temperature of the ammonium halides and at a pressure substantially identical to or lower than the pressure of step b), in order to obtain at least one second gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

According to a variant, step d1) is performed at a temperature of between 200 and 450°C and step d2) is performed at a temperature of greater than or equal to 20°C and less than 200°C.

According to a variant, said process comprises at least one step of pretreating the feedstock comprising a tyre pyrolysis oil, said pretreatment step being carried out upstream of step a) and/or upstream of step b), and comprises an adsorption step and/or a filtration step and/or a centrifugation step and/or a settling step and/or an electrostatic separation step and/or a step of washing with an aqueous solution and/or a gas stripping step.

According to a variant, said process comprises a step e) of fractionating all or part of the hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or all or part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), in order to obtain at least one gas stream, a naphtha cut and at least one middle distillates cut.

According to a variant, said process comprises a hydrocracking step f) carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalytic 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 at least a part of said hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or with at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), and/or else with at least a part of the middle distillates cut obtained from fractionation step e) and a gas stream comprising hydrogen, said hydrocracking reaction section being implemented at an average temperature between 250 and 450°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 first hydrocracked effluent.

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

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

According to a variant, at least a part of the hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c) and/or else at least one of the cuts obtained from fractionation step e) is sent to a steam cracking step g) carried out in at least one pyrolysis furnace at a temperature of between 700 and 900°C and at a pressure of between 0.05 and 0.3 MPa relative.

According to a variant, the process comprises selective hydrogenation step a).

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

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

According to a variant, the product comprises, relative to the total weight of the product:

- a total content of metal elements of less than or equal to 10.0 ppm by weight,
- including a content of iron element of less than or equal to 200 ppb by weight, and/or
- a content of silicon element of less than or equal to 5.0 ppm by weight, and/or
- a sulfur content of less than or equal to 100 ppm by weight, and/or
- a nitrogen content of less than or equal to 100 ppm by weight, and/or
- a content of chlorine element of less than or equal to 10 ppm by weight, and/or
- a mercury content of less than or equal to 5 ppb by weight.

According to a variant, the product comprises a content of biological carbon according to ASTM D6866 of between 1% and 70% by weight.

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

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

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.

According to the present invention, the pressures are absolute pressures, also denoted abs., and are given in MPa absolute (or MPa abs.), unless otherwise indicated.

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

Hereinafter, 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.

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

DETAILED DESCRIPTION

The feedstock

According to the invention, the feedstock comprises at least 5% by weight of a tyre pyrolysis oil having a sulfur content of between 2000 and 15 000 ppm by weight relative to the total weight of the tyre pyrolysis oil.

The feedstock may also comprise any other pyrolysis oil, in particular a plastics and/or solid recovered fuels (SRFs) pyrolysis oil.

In addition, the feedstock may optionally be supplemented with a conventional petroleum feedstock and/or a feedstock resulting from the conversion of biomass.

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*).

Tyres 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.

As for plastics waste, this is generally a mixture of several polymers. This may comprise, alone or as a mixture, (low and/or high density) polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride and polystyrene. Furthermore, depending on the uses, the plastics may contain, in addition to the polymers, other compounds, such as plasticizers, pigments, dyes or else polymerization catalyst residues. Plastic waste may additionally contain, in a minor amount, biomass originating, for example, from household waste.

Solid recovered fuels (SRFs), also called refuse-derived fuel (RDF), are solid non-hazardous wastes prepared with a view to energy upgrading, 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 spent tyres, food by-products (fats, animal meal, and the like), viscose and wood waste, light fractions resulting from shredders (for example from used vehicles, electrical and electronic equipment (WEEE), household and commercial waste, residues from the recycling of various types of waste, including certain municipal wastes, plastic waste, textiles or wood, *inter alia*. SRFs generally contain plastic waste.

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 also be prepared by hydrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

The pyrolysis step is generally carried out at a temperature of between 250°C and 750°C. The pyrolysis step can be carried out under more or less severe conditions.

The low-severity pyrolysis step is carried out at a temperature of between 250°C and 450°C, preferably of between 275°C and 425°C and particularly preferably of between 300°C and 400°C. The low-severity pyrolysis step produces pyrolysis oils rich in mono- and diolefins, and also a significant amount of aromatics, and which may include chlorine compounds.

The high-severity pyrolysis step is carried out at a temperature of between 450°C and 750°C, preferably of between 500°C and 700°C and particularly preferably of 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, vacuum 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 stage(s) in order to improve the cracking of the plastics and/or of the tyres and/or of the SRFs, to produce products of value, to provide a feed for the steam cracking, or combinations thereof. The purge gas can comprise hydrogen (H₂), nitrogen (N₂), steam, product gases or combinations thereof.

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, generally has a range of boiling points of between 40°C and 1000°C, preferably of between 45 and 650°C. The tyre pyrolysis oil generally has a range of boiling points of between 100°C and 1000°C, preferably of between 150°C and 650°C. The plastics pyrolysis oil, which is generally lighter, generally

has a range of boiling points of between 40°C and 700°C, preferably of between 45°C and 550°C.

It is also possible to use just a part of the pyrolysis oil obtained by the pyrolysis, for example a pyrolysis oil which has been topped and/or tailed beforehand by a prefractionation step.

The density of the pyrolysis oil, whether obtained 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 density of the tyre pyrolysis oil, measured at 15°C according to the ASTM D4052 method, is generally of between 0.75 g/cm³ and 1.05 g/cm³, preferably of between 0.80 g/cm³ and 0.98 g/cm³. The density of the plastics and/or SRF pyrolysis oil, measured at 15°C according to the ASTM D4052 method, is generally lower and is generally of between 0.75 and 0.99 g/cm³, preferably of between 0.75 and 0.95 g/cm³.

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, is advantageously in liquid form at ambient temperature and comprises in particular a mixture of hydrocarbon compounds, especially paraffins (n-paraffins and isoparaffins), olefins (mono- and/or diolefins), naphthenes and aromatics. In particular, according to 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, of the naphthenes, of the olefins and of the aromatics is equal to 100% by weight of the hydrocarbon compounds. The tyre pyrolysis oil generally contains a significant content of aromatic compounds, for example a content of aromatic compounds of greater than 30% by weight, preferably greater than 40% by weight, and particularly preferably greater than 50% by weight relative to the weight of the tyre pyrolysis oil.

The tyre pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, may contain 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 preferably varies between 5 and 100 mg/g in the pyrolysis oils.

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, may 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 plastics and/or SRF pyrolysis oil produced from plastic waste and/or SRFs which may contain, in a minor amount, biomass originating, for example, from household waste. The content of biological carbon (according to the C^{14} isotope radiocarbon analytical method according to ASTM D6866) can be of between 0% and 70% by weight, preferably of 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 C^{14} isotope radiocarbon analytical method according to ASTM D6866) of between 20-70% 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 contents of impurities in the pyrolysis oils often depend on the origin of the oil. Thus, tyre pyrolysis oils generally contain more heteroelements than plastics and/or SRF pyrolysis oils, in particular sulfur compounds, but also nitrogen, oxygen and halogen (especially chlorine) compounds. They also contain more metals (especially silicon) in general.

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, can additionally comprise, and usually does comprise, impurities such as metals, especially iron, silicon, and halogen compounds, especially chlorine compounds. These impurities can be present at high contents, for example up to 500 ppm by weight or also 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 also between 1 and 500 ppm by weight of halogen elements. The pyrolysis oil can contain up to 500 ppm by weight or also 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 also between 1 and 500 ppm by weight of chlorine element. The pyrolysis oil can contain up to 50 ppm by weight or also 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 pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, 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 1500 ppm by weight or between 1 and 200 ppm by weight of metal or semi-metal elements. Alkali metals, alkaline earth metals, transition metals, post-transition metals and metalloids can be put into the same category as contaminants of metal nature, referred to as metals or metal or semi-metal elements. In particular, the metals or metal or

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

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, 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 weight or between 1 and 15 500 ppm by weight of heteroelements.

The oxygen 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 oxygen.

The nitrogen compounds are generally present in a content of less than 10 000 ppm by weight and preferably of less than 8000 ppm by weight, and generally between 1 and 10 000 ppm by weight or between 1 and 8000 ppm by weight of nitrogen. Tyre pyrolysis oils are generally more heavily laden with nitrogen compounds than plastics and/or SRF pyrolysis oils. The nitrogen compounds present in a tyre pyrolysis oil are generally present in a content of less than 10 000 ppm by weight and preferably of less than 8000 ppm by weight, and generally between 2000 and 10 000 ppm by weight or between 2500 and 8000 ppm by weight of nitrogen compounds.

The nitrogen compounds present in a plastics pyrolysis oil are generally present in a content of less than 5000 ppm by weight and preferably of less than 2500 ppm by weight, and generally between 5 and 5000 ppm by weight or between 10 and 2500 ppm by weight of nitrogen compounds.

The sulfur content differs greatly depending on the origin of the pyrolysis oil.

The sulfur compounds present in a tyre pyrolysis oil 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 2000 and 15 000 ppm by weight or between 2500 and 12 000 ppm by weight of sulfur compounds, preferably between 3000 and 11 000 ppm by weight of sulfur compounds.

The sulfur compounds present in a plastics pyrolysis oil are generally present in a content of less than 2000 ppm by weight and preferably of less than 500 ppm by weight, and generally

between 5 and 2000 ppm by weight or between 10 and 500 ppm by weight of sulfur compounds.

The pyrolysis oil, whether obtained from tyres, plastics and/or SRFs, can also comprise other impurities, such as heavy metals, for example mercury, arsenic, zinc and lead, for example up to 500 ppb by weight of mercury or of arsenic, and generally between 1 and 300 ppb by weight or between 1 and 200 ppb by weight of heavy metals.

The feedstock of the process according to the invention comprises at least 5% by weight of a tyre pyrolysis oil relative to the total weight of the feedstock. Said feedstock can consist solely of tyre pyrolysis oil(s).

The feedstock can also comprise, in addition to the at least 5% by weight of tyre pyrolysis oil, any other pyrolysis oil, in particular a plastics and/or solid recovered fuels (SRF) pyrolysis oil, in any proportion.

Said feedstock can consist solely of tyre pyrolysis oil(s) and of plastics and/or SRF pyrolysis oil(s). In this case, the feedstock comprises a tyre pyrolysis oil in a content of between 5% and 99% by weight, preferably between 5% and 80% by weight, and particularly preferably between 5% and 50% by weight, and a plastics and/or SRF pyrolysis oil in a content of between 1% and 95% by weight relative to the total weight of the feedstock, preferably between 20% and 95% by weight, and particularly preferably between 50% and 95% by weight.

Said feedstock can comprise at least 50% by weight, preferably between 70% and 100% by weight, of pyrolysis oil, including at least 5% by weight of tyre pyrolysis oil, relative to the total weight of the feedstock, that is to say with preference between 50% and 100% by weight, preferably between 70% and 100% by weight, of pyrolysis oil including at least 5% by weight of tyre pyrolysis oil.

The feedstock of the process according to the invention can additionally 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 tyre pyrolysis oil and optionally the plastics and/or SRF 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.

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 obtained from the conversion of biomass can advantageously be chosen from plant oils, oils from algae or algal oils, fish oils, waste food oils, and fats of plant or animal origin, or mixtures of such feedstocks. Said plant oils can advantageously be crude or completely or partly refined, and can be obtained from plants chosen from rapeseed, sunflower, soya, palm, olive, coconut, coconut kernel, castor oil plant, cotton plant, peanut oil, linseed oil and sea kale oil, and all the oils obtained, for example, from sunflower or rapeseed 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 obtained from the catering industries. Frying oils, various animal oils, such as fish oils, tallow or lard, can also be used. The feedstock obtained from the conversion of biomass can also advantageously be chosen from methyl esters of fatty acids of plant and/or animal origin or also methyl esters of fatty acids from waste edible plant oils.

The feedstock obtained from the conversion of biomass can also be chosen from feedstocks originating from processes for thermal or catalytic conversions of biomass, such as oils which are 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 (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 (optional)

Said feedstock comprising a tyre pyrolysis oil may advantageously be pretreated in at least one optional pretreatment step, prior to the optional selective hydrogenation step a) and/or to hydrogenation step b), in order to obtain a pretreated feedstock which feeds step a) and/or step b).

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

Said optional pretreatment step can be carried out 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 and/or a settling 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 carried out at a temperature 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.

According to a variant, said optional pretreatment step is carried out 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 preferably is devoid of metal elements. Metal elements of the adsorbent should be understood as meaning the elements of 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 can comprise items of equipment which make it possible to bring the feedstock into contact with the aqueous solution and to separate the phases so as to obtain, on the one hand, the pretreated feedstock 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 carried out by filtration. The filtration step makes it possible to remove the inorganic solids, sediments and/or fines contained in the feedstock, 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 different pore sizes, in particular a series of filters having decreasing pore sizes in the direction of the circulation 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.

Whatever the filters, in particular with adjuvants, two filters can be used in parallel in order to carry out unclogging and maintenance on one, while the other is in operation.

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

According to another variant, said optional pretreatment step is carried out 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, thus reducing the probability of formation of free radicals leading to polymerization in the downstream steps. The process generally involves bringing the feedstock into contact with an extraction gas (for example H_2 , N_2 or a mixture thereof), thus transferring at least a portion of the dissolved oxygen of the feedstock or the cut to the extraction gas, followed by the separation of the extraction gas from the feedstock. Any dissolved H_2 remaining in the feedstock after the gas extraction step is not a problem in view of the hydrogenation steps carried out downstream.

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

Said optional pretreatment step thus makes it possible to obtain a pretreated feedstock which subsequently feeds hydrogenation step b) and/or selective hydrogenation step a) when the latter is present.

Selective hydrogenation step a) (optional)

According to the invention, the process optionally comprises a selective hydrogenation step a) carried out in a reaction section employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one selective hydrogenation catalyst, said selective hydrogenation reaction section being fed at least with said feedstock and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature between 100 and 280°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs. and an hourly space velocity between 0.3 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 feedstock 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 feedstock. 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 b) and c). 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 fixed-bed selective hydrogenation, in the presence of at least one selective hydrogenation catalyst, advantageously at an average temperature between 100 and 280°C, with preference between 110 and 250°C, preferably between 130 and 200°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 those 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 thereof, that are used. The average temperature (or WABT) is calculated in the following way:

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

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 flow rate by volume of the feedstock to the volume of catalyst(s).

The amount of the gas stream comprising hydrogen (H₂) feeding said reaction section of step a) is advantageously such that the hydrogen coverage is between 1 and 200 Sm³ of hydrogen per m³ of feedstock (Sm³/m³), with preference between 1 and 150 Sm³ of hydrogen per m³ of feedstock (Sm³/m³), preferably between 5 and 100 Sm³ of hydrogen per m³ of feedstock (Sm³/m³).

The hydrogen coverage is defined as the ratio of the flow rate by volume of hydrogen, taken under standard temperature and pressure conditions, with respect to the flow rate by volume

of the feedstock, without taking into account a recycled fraction, at 15°C (in standard m³, denoted Sm³, of H₂ per m³ of feedstock).

The gas stream comprising hydrogen, which feeds the reaction section of step a), can consist of a supply of hydrogen and/or of recycled hydrogen obtained in particular from the separation step d).

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, referred to with the term PRS for Permutable Reactor System or also "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 FR 2 681 871.

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 3 051 375.

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

The hydro-dehydrogenating 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 the metal elements from groups VIB and VIII (that is to say, the sum of the metal 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 with preference between 1 and 20 and preferably 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 of 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 P_2O_5 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 B_2O_3 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. The alumina used can, for example, be 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 also compounds including a furan ring or also 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 beds with particles of different diameters, in particular a series of guard beds having decreasing diameters in the direction of the circulation 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 feedstock. The selective hydrogenation step a) makes it possible to convert at least 60% and preferably at least 70% of the diolefins contained in the feedstock. The selectively hydrogenated effluent, obtained on conclusion of selective hydrogenation step a), is sent at least in part and preferably entirely, preferably directly, to hydrogenation step b).

Hydrogenation step b)

According to the invention, the process comprises a hydrogenation step b) carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalytic 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 feedstock or said selectively hydrogenated effluent obtained from step a) and a gas stream comprising hydrogen, said hydrogenation reaction section being implemented at an average temperature between 140 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 hydrogenated effluent.

Step b) is in particular carried out under temperature and hydrogen pressure conditions which make it possible to carry out the hydrogenation of the diolefins, possibly remaining after the optional selective hydrogenation step, and of the olefins at the beginning of the hydrogenation reaction section, while making it possible, by an increasing profile of the temperature, to carry out the hydrodemetallization and the hydrodechlorination, in particular at the end of the hydrogenation reaction section. A necessary amount of hydrogen is injected so as to make possible the hydrogenation of at least a part of the diolefins and olefins present in the pyrolysis oil, the hydrodemetallization of at least a part of the metals, notably the retention of silicon, and also the conversion of at least a part of the chlorine (to give HCl). The hydrogenation of the diolefins and olefins 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 olefins and thus the formation of oligomers and polymers, which can plug the reaction section of hydrotreatment step c). In parallel with the hydrogenation, the hydrodemetallization, and in particular the retention of silicon during step b), makes it possible to limit the catalytic deactivation of the reaction section of hydrotreatment step c). Furthermore, the conditions of step b) make it possible to convert at least a part of the chlorine.

A person skilled in the art will readily understand that, in the hydrogenation step b), hydrogenation reactions as described above are carried out but also in parallel some of the other hydrotreatment reactions, and in particular hydrodesulfurization and hydrodenitrogenation reactions, are carried out, even if these reactions are more favoured in the hydrotreatment step c), which is generally carried out at a higher temperature.

The temperature in step b), whether this is the average temperature (WABT), the inlet temperature of the reaction section or else the rise in the temperature in step b) between inlet and outlet of the reaction section, can in particular be controlled by injection of a diluent in step b), preferably of a recycle of a part of the hydrocarbon effluent obtained from step d)

(or d1)) and/or of at least a part of one or more cuts obtained from step e), in particular by the recycle ratio and/or by the temperature of the recycled effluent.

Said reaction section implements a hydrogenation in the presence of at least one hydrogenation catalyst, advantageously at an average temperature (or WABT as defined below) between 140 and 400°C, preferably between 240 and 350°C and particularly preferably between 260 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 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 of step b) is advantageously such that the hydrogen coverage is between 100 and 1500 Sm³ of hydrogen per m³ of feedstock (Sm³/m³), with preference between 200 and 1000 Sm³ of hydrogen per m³ of feedstock (Sm³/m³), preferably between 250 and 800 Sm³ of hydrogen per m³ of feedstock (Sm³/m³).

The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above in step a).

The hydrogen can be obtained from a fossil source or from a renewable source, for example obtained from the gasification of plastic waste, or be produced by electrolysis.

Advantageously, the reaction section of said step b) comprises between 1 and 5 reactors, preferably between 2 and 5 reactors, and particularly preferably it comprises two reactors. The advantage of a hydrogenation reaction section comprising several reactors lies in an optimized treatment of the feedstock, while making it possible to reduce the risks of clogging of the catalytic bed(s) and thus to avoid shutdown of the unit due to clogging.

According to a preferred variant, these reactors operate in permutable mode, known as PRS for Permutable Reactor System, or also "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 FR 2 681 871.

According to a particularly preferred variant, the hydrogenation reaction section of step b) comprises two reactors operating in permutable mode.

The hydrogenation reaction section employing at least one fixed-bed reactor can operate with gas and liquid downflow or upflow.

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 3 051 375.

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

According to a variant, the hydro-dehydrogenating function comprises in particular at least one element from group VIII, preferably chosen from nickel and cobalt, and at least one element from group VIB, 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 metal (or metals) from group VIB relative to the metal (or to the metals) from group VIII is with preference between 1 and 20 and preferably between 2 and 10.

According to this variant, the reaction section of said step b) 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 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, preferably on an alumina support.

According to another variant, the hydro-dehydrogenating function comprises, and preferably consists of, at least one element from group VIII, preferably nickel. According to this 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, 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 hydrogenation catalyst comprises an alumina support, optionally doped with phosphorus and optionally boron. When phosphorus pentoxide P_2O_5 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 B_2O_3 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 can, for example, be a γ (gamma) or η (eta) alumina.

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

Very preferably, step b) can moreover employ, in addition to the hydrogenation catalyst(s) described above, at least one hydrogenation catalyst used in step b) 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 weight of molybdenum and at least 0.1% by weight of molybdenum, preferably 0.5% by weight of molybdenum, expressed as molybdenum oxide MoO_3 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.

Preferably, step b) can employ, upstream of the 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. Use may also be made of a series of guard beds with particles of different diameters, in particular a series of guard beds having decreasing diameters in the direction of the circulation of the feedstock (also referred to as "grading").

Said hydrogenation step b) makes it possible to obtain a hydrogenated effluent, that is to say an effluent having a reduced content of olefins, in particular of diolefins, and of metals, in particular of silicon, and of halogens, in particular of chlorine. The hydrogenation step b) generally makes it possible to convert at least 40% and preferably at least 60% of the diolefins and also at least 40% and preferably at least 60% of the olefins contained in the initial feedstock. The heat given off by the saturation of the double bonds makes it possible to raise the temperature of the reaction medium and to initiate the hydrotreatment reactions, in particular the removal, at least partly, of other contaminants, such as, for example, silicon and chlorine or also nitrogen. Preferably, at least 50% and more preferentially at least 75% of the chlorine and of the silicon of the initial feedstock are respectively removed during step a).

Generally, the silicon content is less than 10 ppm by weight in the hydrogenated effluent of step b).

When separation step d) is carried out after hydrotreatment step c), the hydrogenated effluent obtained on conclusion of hydrogenation step b) is sent at least in part and preferably entirely, preferably directly, to hydrotreatment step c).

When separation step d) is carried out between steps b) and c), the hydrogenated effluent obtained on conclusion of hydrogenation step b) is sent at least in part and preferably entirely, preferably directly, to separation step d).

Hydrotreatment step c)

According to the invention, the treatment process comprises a hydrotreatment step c) carried out in a hydrotreatment reaction section, employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment reaction section being fed at least with said hydrocarbon effluent obtained from step d) when separation step d) is carried out between steps b) and c), and/or at least with the hydrogenated effluent obtained from step b) when separation step d) is carried out after step c), and a gas stream comprising hydrogen, said hydrotreatment reaction section being implemented at an average temperature between 250 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 effluent.

Advantageously, step c) implements the hydrotreatment reactions well known to those skilled in the art, and more particularly hydrotreatment reactions such as the hydrogenation of aromatics, hydrodesulfurization and hydrodenitrogenation. Furthermore, the hydrogenation of the remaining halogen compounds and olefins and also the hydrodemetallization are continued.

Said hydrotreatment reaction section is advantageously implemented at a pressure equivalent to that used in the reaction section of the hydrogenation step b), and generally at a higher average temperature than that of the reaction section of the hydrogenation step b). Thus, said hydrotreatment reaction section is advantageously implemented at an average hydrotreatment temperature between 250 and 430°C, preferably between 280 and 380°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, with preference 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 c) is advantageously between 100 and 1500 Sm³ of hydrogen per m³ of fresh feedstock, and

preferably between 200 and 1000 Sm³ of hydrogen per m³ of fresh feedstock, preferably between 250 and 800 Sm³ of hydrogen per m³ of fresh feedstock. The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above.

Advantageously, the reaction section of said step c) 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 a permutable (or PRS) mode.

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

The hydrotreatment reaction section employing at least one fixed-bed reactor can operate with gas and liquid downflow or upflow.

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

Advantageously, said hydrotreatment catalyst used in said step c) can be chosen from known hydrodemetallization, hydrotreatment or silicon-scavenging catalysts used in particular for the treatment of petroleum-based cuts, and combinations thereof. Known hydrodemetallization catalysts are, for example, those described in patents EP 0 113 297, EP 0 113 284, US 5 221 656, US 5 827 421, US 7 119 045, US 5 622 616 and US 5 089 463. Known hydrotreatment catalysts are, for example, those described in patents EP 0 113 297, EP 0 113 284, US 6 589 908, US 4 818 743 or US 6 332 976. Known silicon-scavenging catalysts are, for example, those described in patent applications CN 102051202 and US 2007/080099.

In particular, said hydrotreatment catalyst comprises a support, preferably a mineral support, and at least one metal element having a hydro-dehydrogenating function. Said metal element having a hydro-dehydrogenating function advantageously comprises at least one element from group VIII, preferably chosen from the group consisting of nickel and cobalt, and/or at least one element from group VIB, 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, 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 metal (or metals) from group VIB relative to the metal (or to the metals) from group VIII is with preference between 1.0 and 20 and preferably between 2.0 and 10. For example, the hydrotreatment reaction section comprises a hydrotreatment catalyst comprising between 0.5% and 10% by weight of nickel, preferably between 1% and 8% by weight of nickel, expressed as nickel oxide NiO relative to the total weight of the hydrotreatment catalyst, and between 1.0% and 30% by weight of molybdenum, preferably between 3.0% and 29% by weight of molybdenum, expressed as molybdenum oxide MoO₃ relative to the total weight of the hydrotreatment catalyst, on a mineral support, preferably on an alumina support.

The support of said hydrotreatment catalyst is advantageously chosen from alumina, silica, silica-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. With preference, said hydrotreatment 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 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 hydrotreatment catalyst is, for example, in the form of extrudates.

Advantageously, said hydrotreatment catalyst of the process has a specific surface area of between 200 and 800 m²/g, with preference of between 250 and 600 m²/g, preferably of between 300 and 400 m²/g. The specific surface area of the hydrotreatment 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 in the journal *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 hydrotreatment catalyst as described above additionally comprises one or more organic compounds containing oxygen and/or nitrogen and/or sulfur as described hereinabove (additivated catalyst).

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

Advantageously, the hydrotreatment 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 b), 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. With preference, the nitrogen content at the outlet of step c) is less than 100 ppm by weight and preferably less than 10 ppm by weight. With preference, the sulfur content at the outlet of step c) is less than 100 ppm by weight and preferably less than 10 ppm by weight. Step c) 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 c) is less than 5 ppm by weight.

The preparation of the catalysts for the selective hydrogenation, hydrogenation, hydrotreatment and hydrocracking steps (see below) is known and generally comprises a step of impregnation of the metals from group VIII and from group VIB, when it is present, and optionally of the phosphorus and/or of the 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 of greater than or equal to 200°C. Before their use in a step of the process, the catalysts are generally subjected to a sulfidation in order to form the active species.

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, of the optional selective hydrogenation step a) and/or of the hydrogenation step b) and/or of the hydrotreatment step c) and/or upstream of one of the optional hydrocracking steps, when they are present, preferably upstream of the hydrogenation step b) and/or the hydrotreatment step c), 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 those skilled in the art, and advantageously under a sulfo-reductive atmosphere in the presence of hydrogen and hydrogen sulfide. The sulfiding agents are preferably H_2S gas, elemental sulfur, CS_2 , mercaptans, sulfides and/or polysulfides, hydrocarbon cuts having a boiling point of less than 400°C and 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, the time that the H_2S is formed. Additional injections throughout the catalytic cycle may be necessary in order to compensate for the natural loss. However, the act of using a tyre pyrolysis oil that is heavily laden with sulfur makes it possible to considerably reduce the consumption of sulfiding agent, or even to completely eliminate the use thereof.

Separation step d)

According to the invention, the treatment process comprises a separation step d), carried out between steps b) and c) and/or after step c), said step being fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c) when separation step d) is carried out after step c), and an aqueous solution, said step being performed in a separation section, in order to obtain at least one gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

This washing/separation step makes it possible in particular to remove the ammonium chloride salts which form by reaction between the chloride ions, released by the hydrogenation of the chlorine compounds in HCl form in particular during the hydrogenation step followed by dissolution in water, and the ammonium ions, generated by the hydrogenation of the nitrogen compounds in the form of NH_3 during the hydrotreatment step and/or supplied by injection of an amine followed by dissolution in water, and thus to limit the risks of plugging, 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 and possibly hydrotreatment step which dissolve in the aqueous solution. When H_2S is present in the hydrotreated effluent obtained from the hydrotreatment step, the washing/separation step also makes it possible to remove ammonium sulfide $((\text{NH}_4)_2\text{S})$ salts which form by reaction between H_2S obtained from the hydrodesulfurization of the sulfur compounds and NH_3 by dissolving them in the aqueous solution.

The washing/separation step is advantageously carried out at a temperature of between 50 and 450°C , preferentially between 100 and 440°C , preferably between 200 and 420°C and particularly preferably between 250 and 420°C . It is important to operate in this temperature range (and therefore not to cool the effluent of the hydrotreatment too much) at the risk of plugging in the lines due to the precipitation of the ammonium chloride salts.

Advantageously, the washing/separation step is carried out at a pressure close to that employed in the hydrogenation step or the hydrotreatment 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 may also be a basic aqueous solution (by adding 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 flash 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 effluent and/or the hydrotreated effluent, upstream of the washing/separation section, so as to dissolve at least some and preferably all of the hydrogen halides (HCl in particular) and any salts present.

In one optional embodiment of the invention, the washing/separation step comprises the injection of an aqueous solution into the hydrogenated effluent and/or the hydrotreated

effluent, followed by the washing/separation section advantageously comprising a separation phase for obtaining at least one aqueous effluent loaded with hydrogen halides (HCl in particular) and any dissolved salts present, said hydrocarbon effluent and a partially washed gaseous effluent. Said aqueous effluent and said hydrocarbon effluent can then be separated in a decanting vessel in order to obtain said washed hydrocarbon effluent 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 hydrogenated and/or 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 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 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 feedstock, a stream containing a nitrogen compound such as ammonia or an amine, for example monoethanolamine, diethanolamine, 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 hydrotreatment step so as to ensure a sufficient amount of ammonium ions for combining the chloride ions formed during the hydrotreatment 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 separation section. The high content of nitrogen compounds in a tyre pyrolysis oil makes it possible to lower or even eliminate the need to add a nitrogen compound.

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

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 only very little chlorine, generally at a content of less than 3 ppm by weight of chlorine, which makes it possible to send it to 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 a), b), c)) and optionally at least one hydrocracking step when such is present), it being possible for the recycling system to comprise a purification section (for example for adsorption of heavy metals, such as mercury).

According to a variant, the separation step d) is carried out after the hydrotreatment step c). When separation step d) is carried out after hydrotreatment step c), the hydrocarbon effluent obtained from separation step d) may be sent, in part or entirely, either directly to the inlet of a steam cracking unit or to an optional fractionation step e). Preferably, the hydrocarbon effluent is sent, in part or entirely, to a fractionation step e). Preferably, the separation step d) is carried out after the hydrotreatment step c).

According to another variant, the separation step d) is carried out between steps b) and c). When separation step d) is carried out between steps b) and c), the hydrocarbon effluent obtained from separation step d) is sent at least in part and preferably entirely, preferably directly, to hydrotreatment step c). This variant is advantageous when the feedstock contains lots of halogen compounds, in particular chlorine compounds. This is because chlorine (in HCl form) contained in the effluent from the hydrogenation step b) may be deposited on the hydrotreatment catalyst of step c), thus leading to a decrease in activity and a decrease in the catalytic cycle time.

According to another variant, the separation step d) can be carried out after step c) and between steps b) and c). In this case, step d) is performed twice. This variant is advantageous for feedstocks that are heavily laden with halogen compounds, and in particular with chlorine compounds.

At least a part of the hydrocarbon effluent obtained from separation step d) when separation step d) is carried out after hydrotreatment step c), and/or at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), can be recycled upstream of step b) and/or step c) and/or also upstream of selective hydrogenation step a). The recycling to or upstream of at least one of the reaction steps advantageously makes it possible, on the one hand, to dilute the impurities and, on the other hand, to control the temperature in the reaction step(s), in which the reactions involved can be highly exothermic. The injection of the recycle stream can be carried out at the level of the first catalytic bed of the reaction section of steps a), b) and/or c) or between the different catalytic beds of each section. When the reaction section comprises two reactors operating in permutable mode, at least a part of the recycle stream can be recycled between the two reactors.

Advantageously, the amount of effluent recycled is adjusted so that the weight ratio between the recycle stream and the feedstock, i.e. the feedstock to be treated feeding the overall process, is less than or equal to 10, preferably less than or equal to 7, and preferentially greater than or equal to 0.001, with preference greater than or equal to 0.01, and preferably greater than or equal to 0.1. Preferably, the amount of recycle is adjusted so that the weight ratio between the recycle stream and the feedstock is between 0.01 and 10, with preference between 0.1 and 7, and particularly preferably between 0.2 and 5.

This recycle ratio it possible in particular to control the rise in temperature in step b). This is because, when the recycle 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 b), in particular due to the hydrogenation reactions of the diolefins, is thus controllable by the dilution effect.

Preferably, an additional gas stream comprising hydrogen is advantageously introduced at the inlet of each reactor, in particular operating in series, and/or at the inlet of each catalytic bed starting from the second catalytic bed of the reaction section. These additional gas streams are also referred to as cooling streams. They make it possible to control the temperature in the reactor in which the reactions carried out are generally highly exothermic. This cooling stream can be injected into the reaction section of step a), b), c) or also f).

According to a preferred variant, at least a part of the recycled effluent can advantageously be either cooled, or preheated, if necessary, or kept at the same temperature as at the outlet of separation step d) when separation step d) is carried out after hydrotreatment step c), and/or as at the outlet of hydrotreatment step c) when separation step d) is carried out between steps b) and c), before reintroducing it into the process according to the invention.

According to a variant, the feedstock, before being preferably mixed with at least a part of the recycled effluent, can be preheated by direct heating to a temperature ranging up to 200°C, preferably up to 180°C and particularly preferably up to 150°C. Above this temperature, contact with a wall during the direct heating can bring about the formation of gums and/or of coke, which can cause fouling and an increase in the pressure drop of the system for heating the feedstock and also of the bed(s) of catalysts, in particular when a selective hydrogenation step a) is not carried out. The heating of the feedstock to a temperature above 150°C, preferably above 180°C and particularly preferably above 200°C is preferably carried out by indirect heating by a hot diluent, preferably by at least a part of the recycled effluent. Thus, the rise in temperature above 150°C, preferably above 180°C and particularly preferably above 200°C of the feedstock is brought about by mixing with a hotter liquid and not by contact with a heated wall. This makes it possible to locally limit the high temperatures. This type of heating by mixing with an inert hot liquid thus makes it possible to limit the

undesirable reactions, such as the polymerization of the diolefins (formation of gum) and/or the formation of coke, and to adjust the inlet temperature of the stream in step b), so as to initiate the reaction of hydrogenation of the unsaturations, preferably at a temperature which is as low as possible, while controlling the exothermicity of these reactions by an effect of dilution of the reactive species.

According to another variant, the feedstock is entirely heated by indirect heating by at least a part of the recycled effluent. In this case, the feedstock is not preheated before being mixed with at least a part of the recycled effluent.

Another heating stream advantageously consists of a hydrogen-rich gaseous effluent originating from the hydrogen supply and/or of the gaseous effluent obtained from the separation step d).

Variant two-step separation step d)

In one possible embodiment of the invention, separation step d), which may be carried out after step c) and/or between steps b) and c), can comprise two steps, a first step of "hot" separation followed by a second step of "cold" separation.

This embodiment makes it possible, via the combination of hot separation step d1) followed by cold separation/washing step d2), to ingeniously remove the chlorine in the form of ammonium chloride salts. Chloride ions, released by the hydrogenation of chlorine compounds in the form of HCl during steps b) and c) (hydrodechlorination), and ammonia, generated by the hydrogenation of nitrogen compounds in the form of NH_3 during step c) in particular (hydrodenitrogenation), largely leave in the gaseous effluent by virtue of the hot separation of step d1). This is because the high temperature of this separation step d1) prevents the precipitation of ammonium chloride salts which form by reaction between chloride ions and ammonium ions. The separation at a lower temperature in step d2) of the gaseous effluent and of a part of the liquid effluent brings about the precipitation of these ammonium chloride salts. The washing with water of this step d) makes it possible to dissolve these salts in the aqueous effluent. A hydrocarbon effluent freed of chlorine is thus obtained.

According to this embodiment, separation step d) can comprise the following steps: d1) a separation step, fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c) when separation step d) is carried out after step c), said step being performed at a temperature greater than the precipitation temperature of the

ammonium halides and at a pressure substantially identical to the pressure of step b) in order to obtain at least one first gaseous effluent and a liquid effluent of which a part is optionally recycled, as recycled effluent, upstream of step b),

d2) a separation step, fed with the first gaseous effluent and optionally at least a part of the liquid effluent obtained from step d1), and an aqueous solution, said step being performed at a temperature lower than the precipitation temperature of the ammonium halides and at a pressure substantially identical to or lower than the pressure of step b), in order to obtain at least one second gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

When separation step d) is carried out after step c) and between steps b) and c), in particular a (first) "hot" separation step d1) (without step d2)) can be carried out, followed by a (second) separation step d1) and/or d2) after step c). Thus, obtained at the first "hot" separation d1) between steps b) and c) are at least one first gaseous effluent and a liquid effluent of which a part is recycled, as recycled effluent, upstream of step b). The gaseous effluent and the other part of the liquid effluent are then introduced into hydrotreatment step c). The hydrotreated effluent is then treated according to step d2) ("cold" separation with washing), optionally supplemented with a step d1) after step c). This configuration has the advantage of obtaining a hot recycle which makes it possible to preheat the feedstock and to control the exothermicity of this step b) while requiring just one washing operation (after step c)) for removing the salts.

Hot separation step d1)

The elevated temperature of this separation step d1) avoids the precipitation of ammonium halide salts which form by reaction between the halide ions and the ammonium ions, in order to recover a gaseous effluent containing the majority of the halides in hydrogen halide (HCl) forms and gaseous ammonia, and a liquid effluent containing very little halides and ammonia.

The term "precipitation temperature" of the ammonium halides is understood to mean the temperature (under given conditions, such as the concentration and the pressure) at which the gaseous ammonia and the hydrogen halides precipitate, either by reacting to form solid crystals of ammonium halides or by dissolving in water. The precipitation temperature depends on the concentrations of halides and on the pressure according to thermodynamic principles. The precipitation temperature of ammonium halides generally lies between 150 and 300°C, often between 180 and 295°C, and particularly between 200° and 290°C, under the conditions of use of the present process.

The temperature at which the separation of step d1) is carried out must be greater than the precipitation temperature of the ammonium halides in order to recover a gaseous effluent containing the majority of the halides in hydrogen halide (HCl) forms and gaseous ammonia, and a liquid effluent containing very little halides and ammonia. The temperature at which the separation of step d1) is carried out is generally of between 200 and 450°C, preferably of between 220 and 330°C and particularly preferably of between 240 and 300°C.

The term "pressure substantially equal to the pressure of step b)" is understood to mean the pressure of step b) with a pressure difference of between 0 and 1 MPa, preferably of between 0.005 and 0.3 MPa and particularly preferably of between 0.01 and 0.3 MPa, with respect to the pressure of step b). Preferably, the pressure of step d1) is the pressure of step b) decreased by the pressure drops.

Separation step d1) can advantageously be carried out by any method known to those skilled in the art, such as, for example, the combination of one or more separators (drums) and/or one or more stripping columns, 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, step d1) is carried out with a single separator (drum).

The separation step d1) is a separation step referred to as a high-pressure or medium-pressure high-temperature separation step, also known to those skilled in the art under the name HHPS (Hot High Pressure Separator). Thus, this step d1) preferably employs a "hot high-pressure" separator, the pressure being substantially equal to the operating pressure of step b).

The gas/liquid separation has an efficiency corresponding to the solubility and to Henry's law. This means that an equilibrium amount of halides in the forms of hydrogen halides will remain in the liquid effluent obtained in step d1). These halides will be released in the gaseous effluent during the cold separation step d2) and then discharged by dissolution in the aqueous effluent.

Advantageously, a part of the liquid effluent from step d1) is recycled upstream of step b) and/or optionally upstream of step a) as recycled effluent in the recycle amounts described above. Aside from the advantages of dilution of impurities and temperature control as described above, the recycle allows in particular an indirect heating of the feedstock or selectively hydrogenated effluent by simply mixing the "cold" feedstock or the "cold" selectively hydrogenated effluent with the hot recycle.

According to a preferred variant, at least a part of the recycled effluent can advantageously be either cooled, or preheated, if necessary, or kept at the same temperature as at the outlet

of separation step d1) when separation step d) is carried out after hydrotreatment step c), and/or as at the outlet of hydrotreatment step c) when separation step d) is carried out between steps b) and c), before reintroducing it into the process according to the invention.

The high-pressure and high-temperature separation makes it possible, on the one hand, to maximize the recovery of energy by the hot recycle of a part of the liquid effluent. This is because the energy in order to reach the inlet temperature necessary in step b), and/or optionally in step a), is at least partly contributed by the heat of a part of the recycled effluent obtained from step d1) and also makes it possible to reduce, indeed even eliminate, an optional preheating by direct heating of the feedstock beyond a temperature of greater than 200°C in order to prevent the formation of gums. Furthermore, the act of recycling preferably at least a part of the liquid effluent at high pressure makes it possible to save on energy for the pressurization thereof in step b).

The separation at high pressure and high temperature also makes it possible to minimize the amount of light fraction (naphtha cut) contained in the liquid effluent. At this temperature, virtually all of the light fraction of the effluent (naphtha) leaves as gaseous effluent to the cold separation/washing step d2), while, as liquid phase, there is predominantly the heavy fraction of the feedstock (middle distillates cut). During a recycling of a part of the liquid effluent to step b), the H2pp is favoured in step b) because the light fraction (naphtha) might partly vaporize and lower the H2pp if it were not at least partly removed during the high-pressure and high-temperature separation. The removal of the light fraction comprising naphtha can optionally be increased by a slight pressure reduction upstream of at least one separator used in step d2), even if this use is not preferred as a result of the energy loss associated with the pressure reduction. Another option for increasing the removal of the light fraction comprising naphtha can consist in carrying out a stripping, for example by injecting a hydrogen-rich gas in step d1).

Cold separation and washing step d2)

According to the invention, the treatment process can comprise a separation step d2), fed with the first gaseous effluent and optionally at least a part of the liquid effluent obtained from step d1) and an aqueous solution, said step being performed at a temperature lower than the precipitation temperature of the ammonium halides and at a pressure substantially identical to or lower than the pressure of step b), in order to obtain at least one second gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

The separation of step d2) at a temperature lower than the precipitation temperature of the ammonium halides of the gaseous effluent and optionally at least a part of the liquid effluent obtained from step d1) causes precipitation of the ammonium halide salts which form by

reaction between the halide ions and the ammonium ions contained in particular in the gaseous effluent.

Cold separation step d2) is fed with the gaseous effluent alone obtained from step d1) or with the mixture of gaseous effluent and at least a part of the liquid effluent which are obtained from step d1). Preferably, the cold separation step d2) is fed with the mixture of gaseous effluent and at least a part of the liquid effluent. According to a variant, the cold separation step d2) is fed with the mixture of gaseous effluent and the entirety of the liquid effluent. The act of carrying out cold separation step d2) on the mixture of gaseous effluent and liquid effluent has the advantage of extracting not just the contaminants from the gaseous effluent but also the hydrogen halides (HCl) dissolved in the liquid effluent. Specifically, the hydrogen halides dissolved in the liquid effluent obtained from step d1) are released and also form ammonium halides with the ammonia present in the gaseous effluent.

The washing with an aqueous solution of this step d2) makes it possible to dissolve these salts in the aqueous effluent. A hydrocarbon effluent freed of halides, a gaseous effluent freed of halides and an aqueous effluent in which the ammonium halide salts are dissolved are thus obtained.

The temperature at which the separation of step d2) is carried out should be lower than the precipitation temperature of the ammonium halides in order to cause the ammonium halide salts to precipitate. The temperature at which the separation of step d2) is carried out is greater than or equal to 20°C and less than 200°C, preferably of between 25 and 120°C and particularly preferably of between 30 and 70°C.

The term "pressure substantially equal to the pressure of step b)" is understood to mean the pressure of step b) with a pressure difference of between 0 and 1 MPa, preferably of between 0.005 and 0.3 MPa and particularly preferably of between 0.01 and 0.3 MPa, with respect to the pressure of step b). Preferably, the pressure of step d2) is the pressure of step b) decreased by the pressure drops. The act of operating at least a part of separation step d2) at a pressure substantially identical to the operating pressure of step b) furthermore facilitates the recycling of hydrogen contained in the gaseous effluent.

Separation step d2) can also be carried out at a lower pressure than the pressure of step b).

Separation step d2) can also comprise a (first) step of separation at a pressure substantially equal to the operating pressure of step b), followed by at least one other step of separation performed at a temperature identical to or lower than and at a pressure lower than each preceding separation step of step d2).

Separation step d2) can advantageously be carried out by any method known to those skilled in the art, such as, for example, the combination of one or more separators (drums) and/or one or more stripping columns, 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. Separation step d2) can, for example, comprise a column for stripping sour water (also known as sour water stripper) from the withdrawn aqueous effluent, a column for washing sour gases in order to purify the hydrogen-rich gas before recycling, a column for stabilization of the washed liquid effluent in order to remove the dissolved gases.

Preferably, step d2) is carried out with a single separator (drum). The separation step d2) is preferably carried out in at least one separator drum referred to as a high-pressure or medium-pressure low-temperature separator drum, also known to a person skilled in the art under the name CHPS (Cold High Pressure Separator). Thus, this step d2) preferably employs a "cold high-pressure" separator, the pressure being substantially equal to the operating pressure of step b).

Fractionation step e) (optional)

The process according to the invention can comprise a step of fractionating all or part, preferably the entirety, of the hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or all or part, preferably the entirety, of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps a) and c), in order to obtain at least one gas stream, a naphtha cut and at least one middle distillates cut.

The term "naphtha cut" is understood to mean a hydrocarbon cut comprising compounds having a boiling point generally of less than or equal to 175°C, in particular between 80°C and 175°C.

The term "middle distillates cut" is understood to mean a hydrocarbon cut comprising compounds having a boiling point generally of greater than 175°C. The heavy cut may include middle distillates such as a diesel cut and/or a kerosene cut. It may also comprise heavier compounds.

Depending on the destination or the use of the cuts obtained from the fractionation step e), a person 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, 175 or 200°C, or even 250°C.

Step e) makes it possible in particular to remove the gases dissolved in the hydrotreated liquid effluent, such as, for example, ammonia, hydrogen sulfide and light hydrocarbons having from 1 to 4 carbon atoms.

The optional fractionation step e) 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.

According to one embodiment, step e) can be performed in a section advantageously comprising at least one stripping column equipped with a reflux circuit comprising a reflux drum. Thus, the lightest compounds are entrained in the column top and into the reflux circuit comprising a reflux drum in which a gas/liquid separation is performed. The gas phase which comprises the light hydrocarbons is withdrawn from the reflux drum as a gas stream. The naphtha cut is advantageously withdrawn from the reflux drum as a liquid stream. The middle distillates cut is advantageously withdrawn from the bottom of the stripping column.

According to another embodiment, step e) can be performed in a section comprising one or more separator drums. Advantageously, use will be made of at least one "low-pressure low-temperature" separator drum in order to remove the gases dissolved in the hydrotreated liquid effluent.

According to other embodiments, fractionation step e) can employ a stripping column or a separator drum followed by a distillation column or only a distillation column.

The naphtha cut and middle distillates cut, which are optionally mixed, can be sent, in full or in part, to a steam cracking unit, at the outlet of which olefins may be (re)formed in order to participate in the formation of polymers. Preferably, only a part of said cuts is sent to a steam cracking unit; at least a fraction of the remaining part is optionally recycled into at least one of the steps of the process and/or sent to a fuel storage unit, for example a unit for storage of naphtha, a unit for storage of diesel or a unit for storage of kerosene, resulting from conventional petroleum-based feedstocks.

According to a preferred embodiment, the naphtha cut, in full or in part, is sent to a steam cracking unit, while the middle distillates cut is sent to a hydrocracking step f) and/or sent to a fuel storage unit.

In a particular embodiment, the optional fractionation step e) may make it possible to obtain, besides a gas stream, a naphtha cut (generally comprising compounds having a boiling point of less than or equal to 175°C, preferably between 80 and 175°C), and a middle distillates cut (generally comprising compounds having a boiling point of greater than 175°C and less

than 385°C), and a heavy hydrocarbon cut (generally comprising compounds having a boiling point of greater than or equal to 385°C). The naphtha cut can be sent, in full or in part, to a steam cracking unit and/or to the unit for storage of naphtha resulting from conventional petroleum feedstocks; it can also be recycled; the middle distillates cut can also be, in full or in part, either sent to a steam cracking unit, or to a unit for storage of diesel resulting from conventional petroleum feedstocks, or to hydrocracking step f) when this is present, or also be recycled; the heavy cut can, for its part, be sent, at least in part, to a steam cracking unit or be sent to the hydrocracking step when this is present.

In another particular embodiment, the optional fractionation step e) may make it possible to obtain, besides a gas stream, a naphtha cut (generally comprising compounds having a boiling point of less than or equal to 175°C, preferably between 80 and 175°C), and a kerosene cut (generally comprising compounds having a boiling point of greater than 175°C and less than or equal to 280°C), a diesel cut (generally comprising compounds having a boiling point of greater than 280°C and less than 385°C), and a heavy hydrocarbon cut (generally comprising compounds having a boiling point of greater than or equal to 385°C). The naphtha cut, the kerosene cut and/or the diesel cut can be, in full or in part, either sent to a steam cracking unit, or respectively to a naphtha, kerosene or diesel pool resulting from conventional petroleum feedstocks, or be recycled. The diesel and/or kerosene cuts can also be sent to hydrocracking step f) when this is present. The heavy cut can, for its part, be sent, at least in part, to a steam cracking unit, or be sent to hydrocracking step f) when this is present.

In another particular embodiment, the naphtha cut obtained from step e) is fractionated into a heavy naphtha cut (generally comprising compounds having a boiling point between 80 and 175°C) and a light naphtha cut (generally comprising compounds having a boiling point of less than 80°C), at least a part of said heavy naphtha cut being sent to an aromatics complex comprising at least one step of reforming of the naphtha for the purpose of producing aromatic compounds. According to this embodiment, at least a part of the light naphtha cut is sent to the steam cracking step g) described below.

When the content of tyre pyrolysis oil is high in the feedstock (i.e. greater than 50% by weight of the feedstock), the naphtha cut obtained from the process according to the invention can also be sent to a catalytic reforming unit. This is because the high content of aromatics in tyre pyrolysis oils makes it possible to obtain a highly aromatic and naphthenic naphtha cut which has a high octane number (high RON/MON (RON = Research Octane Number and Motor Octane Number)).

The gaseous effluent(s) obtained from fractionation step e) can be subject to additional purification(s) and separation(s) for the purpose of recovering at least light hydrocarbons, in particular ethane, propane and butane, which can advantageously be sent, separately or as a mixture, to one or more furnaces of steam cracking step g) so as to increase the overall yield of olefins.

Hydrocracking step f) (optional)

According to a variant, the process of the invention can comprise a step f) of hydrocracking with at least a part of said effluent obtained from step d) when separation step d) is carried out after step c), and/or with at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), and/or else with at least a part of the middle distillates cut obtained from fractionation step e).

Advantageously, step f) implements hydrocracking reactions well known to those skilled in the art, and more particularly makes it possible to convert the heavy compounds, for example compounds having a boiling point of greater than 175°C, into compounds having a boiling point of less than or equal to 175°C. Other reactions, such as hydrogenation of olefins, aromatics, hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, and the like, may continue.

The compounds having a boiling point of greater than 175°C contain, compared 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 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.

Thus, the process of the invention can comprise a hydrocracking step f) carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalytic 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 at least a part of said effluent obtained from step d) when separation step d) is carried out after step c), and/or with at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), and/or else with at least a part of the middle distillates cut obtained from fractionation step e) and a gas stream comprising hydrogen, said hydrocracking reaction section being implemented at an average temperature between 250

and 450°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 first hydrocracked effluent.

Thus, said hydrocracking reaction section is advantageously implemented at an average temperature between 250 and 480°C, preferably between 320 and 450°C, at a hydrogen partial pressure between 1.5 and 20.0 MPa abs., preferably between 3 and 18.0 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 4 h⁻¹. The hydrogen coverage in step f) is advantageously between 80 and 2000 Sm³ of hydrogen per m³ of fresh feedstock which feeds step f) and preferably between 200 and 1800 Sm³ of hydrogen per m³ of fresh feedstock which feeds step f). The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above.

Advantageously, said hydrocracking reaction section is implemented at a pressure equivalent to that used in the reaction section of the hydrogenation step b) or the hydrotreatment step c).

Advantageously, said step f) is carried out in a hydrocracking reaction section comprising at least one, preferably between one and five, fixed-bed reactor(s) having n catalytic beds, n being an integer greater than or equal to one, with preference of between one and ten, preferably of between two and five, said bed(s) each comprising at least one, and preferably not more than ten, hydrocracking catalyst(s).

The hydrocracking reaction section employing at least one fixed-bed reactor can operate with gas and liquid downflow or upflow.

The hydrocracked effluent can be recycled at least in part into steps b), c), d) or e).

The hydrocracking step can be carried out in one step (step f)) or two steps (steps f) and f')). When it is carried out in two steps, a separation of the effluent obtained from the first hydrocracking step f) is carried out, making it possible to obtain a hydrocarbon cut comprising compounds having a boiling point of greater than 175°C (middle distillates cut), which cut is introduced into the second hydrocracking step f') comprising a dedicated second hydrocracking reaction section different from the first hydrocracking reaction section f). This configuration is particularly suitable when it is desired to produce only a naphtha cut.

The second hydrocracking step f') is carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalytic 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 at least a part of the first hydrocracked effluent obtained from

the first hydrocracking step f) and a gas stream comprising hydrogen, said hydrocracking reaction section being implemented at an average temperature between 250 and 450°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 second hydrocracked effluent. 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.

Said second hydrocracking step is preferably carried out in a hydrocracking reaction section comprising at least one, preferably between one and five, fixed-bed reactor(s) having n catalytic beds, n being an integer greater than or equal to one, with preference of between one and ten, preferably of between two and five, said bed(s) each comprising at least one, and preferably not more than ten, hydrocracking catalyst(s).

These operating conditions used in the hydrocracking step(s) generally make it possible to obtain conversions per pass, into products having at least 80% by volume of compounds having boiling points of less than or equal to 175°C, with preference of less than 160°C and preferably of less than 150°C, and of greater than 15% by weight and more preferably still of between 20% and 95% by weight. When the process is carried out in two hydrocracking steps, the conversion per pass in the second step is kept moderate in order to maximize the selectivity for compounds of the naphtha cut (with a boiling point of less than or equal to 175°C, in particular between 80 and less than or equal to 175°C). The conversion per pass is limited by the use of a high recycle ratio over the loop of the second hydrocracking step. This ratio is defined as the ratio of the feed flow rate of step f) to the flow rate of the feedstock of step b); preferentially, this ratio is between 0.2 and 4, preferably between 0.5 and 2.5.

The hydrocracked effluent from the second hydrocracking step f') can be recycled at least in part into steps b), c), d) or e).

The hydrocracking step(s) thus do not necessarily make it possible to convert all the hydrocarbon compounds of the middle distillates cut into hydrocarbon compounds having a boiling point of less than or equal to 175°C (naphtha cut). After the fractionation step e), there may thus remain a more or less significant proportion of compounds having a boiling point of greater than 175°C. At least a part of this unconverted cut can be introduced into a second hydrocracking step f'). Another part can be bled off. Depending on the operating conditions of the process, said bleed can be of between 0% and 10% by weight of the cut comprising compounds having a boiling point of greater than 175°C, relative to the incoming feedstock, and preferably between 0.5% and 5% by weight.

In accordance with the invention, the hydrocracking step(s) proceed(s) in the presence of at least one hydrocracking catalyst.

The hydrocracking catalyst(s) used in the hydrocracking step(s) are conventional hydrocracking catalysts known to those skilled in the art, of bifunctional type combining an acid function with a hydro-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 aluminum and boron oxides, amorphous silica-aluminas and zeolites. The hydro-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.

Preferably, the hydrocracking catalyst(s) comprise a hydro-dehydrogenating function comprising at least one metal from group VIII chosen from iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum, and preferably from cobalt and nickel. Preferably, said catalyst(s) also comprise at least one metal from group VIB chosen from chromium, molybdenum and tungsten, alone or as a mixture, and preferably from molybdenum and tungsten. Hydro-dehydrogenating functions of NiMo, NiMoW or NiW type are preferred.

Preferably, the content of metal from group VIII in the hydrocracking catalyst(s) is advantageously of between 0.5% and 15% by weight and preferably between 1% and 10% by weight, the percentages being expressed as percentage by weight of oxides 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.

Preferably, the content of metal from group VIB in the hydrocracking catalyst(s) is advantageously of between 5% and 35% by weight and preferably between 10% and 30% by weight, the percentages being expressed as percentage by weight of oxides relative to the total weight of the catalyst. When the metal is molybdenum or tungsten, the metal content is expressed as MoO₃ and WO₃ respectively.

The hydrocracking catalyst(s) can also optionally comprise at least one promoter element deposited on the catalyst and chosen from the group formed by phosphorus, boron and silicon, optionally at least one element from group VIIA (chlorine, fluorine preferred), optionally at least one element from group VIIB (manganese preferred) and optionally at least one element from group VB (niobium preferred).

Preferably, the hydrocracking catalyst(s) comprise at least one amorphous or poorly crystalline porous mineral matrix of oxide type chosen from aluminas, silicas, silica-aluminas, aluminates, alumina-boron oxide, magnesia, silica-magnesia, zirconia, titanium oxide or clay, alone or as a mixture, and preferably aluminas or silica-aluminas, alone or as a mixture.

Preferably, the silica-alumina contains more than 50% by weight of alumina, preferably more than 60% by weight of alumina.

Preferably, the hydrocracking catalyst(s) also optionally comprise a zeolite chosen from Y zeolites, preferably from USY zeolites, alone or in combination with other zeolites from beta, ZSM-12, IZM-2, ZSM-22, ZSM-23, SAPO-11, ZSM-48 or ZBM-30 zeolites, alone or as a mixture. Preferably, the zeolite is USY zeolite alone.

In the case where said catalyst comprises a zeolite, the content of zeolite in the hydrocracking catalyst(s) is advantageously of between 0.1% and 80% by weight, preferably of between 3% and 70% by weight, the percentages being expressed as percentage of zeolite relative to the total weight of the catalyst.

A preferred catalyst comprises, and preferably consists of, at least one metal from group VIB and optionally at least one non-noble metal from group VIII, at least one promoter element, and preferably phosphorus, at least one Y zeolite and at least one alumina binder.

An even more preferred catalyst comprises, and preferably consists of, nickel, molybdenum, phosphorus, a USY zeolite, and optionally also a beta zeolite, and alumina.

Another preferred catalyst comprises, and preferably consists of, nickel, tungsten, alumina and silica-alumina.

Another preferred catalyst comprises, and preferably consists of, nickel, tungsten, a USY zeolite, alumina and silica-alumina.

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

In a variant, the hydrocracking catalyst employed in the second hydrocracking step comprises a hydro-dehydrogenating function comprising at least one noble metal from group VIII chosen from palladium and platinum, alone or as a mixture. The content of noble metal from group VIII is advantageously of between 0.01% and 5% by weight and preferably between 0.05% and 3% by weight, the percentages being expressed as percentage by weight of oxides (PtO or PdO) relative to the total weight of the catalyst.

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

Said hydrocarbon effluent or said hydrocarbon cut(s) thus obtained by treatment according to the process of the invention has/have a composition compatible with the specifications of a

feedstock at the inlet of a steam cracking unit. In particular, the composition of the hydrocarbon effluent or said hydrocarbon cut(s) obtained from the process is preferably such that:

- the total content of metal elements is less than or equal to 10.0 ppm by weight, with preference less than or equal to 2.0 ppm by weight, preferentially less than or equal to 1.0 ppm by weight and preferably less than or equal to 0.8 ppm by weight, with:

a content of silicon (Si) element of less than or equal to 5.0 ppm by weight, with preference of less than or equal to 1 ppm by weight and preferably of less than or equal to 0.6 ppm by weight and

a content of iron (Fe) element of less than or equal to 200 ppb by weight,

- the sulfur content is less than or equal to 500 ppm by weight, preferably less than or equal to 200 ppm by weight,

- the nitrogen content is less than or equal to 100 ppm by weight, with preference less than or equal to 50 ppm by weight, preferably less than or equal to 10 ppm by weight, and particularly preferably less than or equal to 5 ppm by weight

- the total content of chlorine element is less than or equal to 5.0 ppm by weight, preferably less than 1.0 ppm by weight,

- the content of olefinic compounds (mono- and diolefins) is less than or equal to 5.0% by weight, with preference less than or equal to 2.0% by weight and preferably less than or equal to 0.1% by weight.

- the mercury content is less than or equal to 5 ppb by weight, preferably less than 3 ppb 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.

The process according to the invention thus makes it possible to treat pyrolysis oils in order to obtain at least one effluent which can be injected, in full or in part, into at least one steam cracking unit.

Steam cracking step g) (optional)

At least a part of the effluent obtained from step d) when separation step d) is carried out after step c), and/or at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c) and/or else at least one of the liquid hydrocarbon cuts obtained from optional fractionation step e), can be sent in part or in full to a steam cracking step g).

Advantageously, the gaseous effluent(s) obtained from the separation step d) and/or the fractionation step e) and containing ethane, propane and butane can also be sent, in full or in part, to the steam cracking step g).

Said steam cracking step g) is advantageously carried out in at least one pyrolysis furnace at a temperature of between 700 and 900°C, preferably between 750 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 optional steam cracking step g) and 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 step g). Preferably, the optional step g) is carried out in several pyrolysis furnaces in parallel, so as to adapt the operating conditions to the various streams feeding step g), in particular obtained from step e), and also to manage the decoking times of the tubes. A furnace comprises one or more tubes arranged in parallel. A furnace can also denote a group of furnaces operating in parallel. For example, a furnace may be dedicated to cracking the middle distillates 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 g) comprises the steam cracking furnaces but also the substeps associated with the steam cracking that are well known to those skilled in the art. These substeps can in particular comprise 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, in particular 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 g) 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, especially 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.

Heavy metal adsorption step (optional)

Any gaseous effluent and/or any liquid effluent obtained from at least one of the separation steps d) or from the fractionation step e) can be subjected to an optional step of adsorption of heavy metals.

The optional adsorption step makes it possible to eliminate 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. The transformed form thereof is easier to trap. Their elimination or reduction may in particular be necessary when a part 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 steps, such as the fractionation step e), 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 obtained 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 and 250°C, preferably between 40 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 adsorbent comprising a porous support, and optionally at least one active phase which can be based on sulfur in the elemental form, or in the metal sulfide or metal oxide form, or also in the metal form in elemental form.

The porous support can be chosen without distinction from the families of the aluminas, silica-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 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 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
Content of Chlorine	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 THE FIGURES

The particulars of the elements referenced in Figures 1 to 4 makes possible a better understanding of the invention, without the latter being limited to the specific embodiments illustrated in Figures 1 to 4. The various embodiments presented can be used alone or in combination with one another, without limitation of combination.

Figures 1 and 2 refer to the embodiment in which separation step d) is carried out after hydrotreatment step c).

Figures 3 and 4 refer to the embodiment in which separation step d) is carried out between hydrogenation step b) and hydrotreatment step c).

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

- an (optional) step a) of selective hydrogenation of a feedstock 1 comprising at least 5% by weight of a tyre pyrolysis oil relative to the total weight of the feedstock, said tyre pyrolysis oil having a sulfur content of between 2000 and 10 000 ppm by weight relative to the total weight of the oil, in the presence of a hydrogen-rich gas 2, in order to obtain a selectively hydrogenated effluent 3;
- a step b) of hydrogenation of said selectively hydrogenated effluent 3 obtained from step a) in the presence of a hydrogen-rich gas 4 and optionally of an amine supplied by the stream 5 and optionally of a sulfiding agent supplied by the stream 6, in order to obtain a hydrogenated effluent 7;
- a hydrotreatment step c) fed with the hydrogenated effluent 7 obtained from hydrogenation step b) and with a stream of a hydrogen-rich gas 8, in order to obtain a hydrotreated effluent 9;
- a separation step d) fed with the effluent 9 obtained from hydrotreatment step c) and in the presence of an aqueous solution 12 in order to obtain at least one gaseous effluent 13, an aqueous effluent 14 and a hydrocarbon effluent 15.

Figure 2 represents the diagram of another particular embodiment of the process of the present invention which is based on the diagram of Figure 1. This diagram comprises a step d) carried out in two steps, steps d1) and d2), followed by a fractionation step e) and additionally a hydrocracking step f).

(Optional) selective hydrogenation step a), hydrogenation step b) and hydrotreatment step c) are carried out as described in Figure 1. Separation step d), carried out in two steps, comprises in particular:

- a step d1) of separation of the hydrotreated effluent 9, carried out at high pressure and high temperature (HHPS), in order to obtain at least one first gaseous effluent 10 and a liquid effluent 11 a part 11a of which can be recycled upstream of step b) or upstream of step a) (not shown),
- a step d2) of separation carried out at high pressure and low temperature (CHPS) and fed with the gaseous effluent 10 and the other part of the liquid effluent 11b obtained from step d1) and an aqueous solution 12 and making it possible to obtain at least one gaseous effluent 13 comprising hydrogen, an aqueous effluent 14 containing dissolved salts and dissolved H_2S and NH_3 , and a hydrocarbon effluent 15;

Optionally, a step e) of fractionation of the effluent 15 is carried out, making it possible to obtain at least one gaseous effluent 16, a naphtha cut 17 and a middle distillates cut 18. On conclusion of step e), a part of the naphtha cut 17 can be sent to a steam cracking process (not illustrated). Another part of naphtha cut 17 can feed selective hydrogenation step a), hydrogenation step b) and/or hydrotreatment step c) (recycling not illustrated).

In Figure 2, at least a part of middle distillates cut 18 obtained from step e) feeds a hydrocracking step f) which is carried out in at least one fixed-bed reactor comprising at least one hydrocracking catalyst and is fed with hydrogen 19. The hydrocracked effluent 20 can be recycled between separation steps d1) and d2) or also upstream of separation step d) (not illustrated).

Figure 3 represents the diagram of a particular embodiment of the process of the present invention, comprising:

- an (optional) step a) of selective hydrogenation of a feedstock 1 comprising at least 5% by weight of a tyre pyrolysis oil relative to the total weight of the feedstock, said tyre pyrolysis oil having a sulfur content of between 2000 and 10 000 ppm by weight relative to the total weight of the oil, in the presence of a hydrogen-rich gas 2, in order to obtain a selectively hydrogenated effluent 3;
- a step b) of hydrogenation of said selectively hydrogenated effluent 3 obtained from step a) in the presence of a hydrogen-rich gas 4 and optionally of an amine supplied by the stream 5 and optionally of a sulfiding agent supplied by the stream 6, in order to obtain a hydrogenated effluent 7;
- a separation step d) fed with the hydrogenated effluent 7 obtained from hydrogenation step b) and in the presence of an aqueous solution 12 in order to obtain at least one gaseous effluent 13, an aqueous effluent 14 and a washed hydrocarbon effluent 23 freed in particular of chlorine impurities;
- a hydrotreatment step c) fed with the washed hydrogenated effluent 23 freed in particular of chlorine impurities and obtained from separation step d) and with a stream of a hydrogen-rich gas 8, in order to obtain a hydrotreated hydrocarbon effluent 15.

Figure 4 represents the diagram of another particular embodiment of the process of the present invention which is based on the diagram of Figure 3. This diagram comprises a step d) carried out in two steps, steps d1) and d2), followed by a fractionation step e) and additionally a hydrocracking step f).

(Optional) selective hydrogenation step a) and hydrogenation step b) are carried out as described in Figure 3. Separation step d), carried out in two steps, comprises in particular:

- a step d1) of separation of the hydrogenated effluent 7, carried out at high pressure and high temperature (HHPS), in order to obtain at least one first gaseous effluent 21 and a liquid effluent 22 a part 22a of which can be recycled upstream of step b) or upstream of step a) (not shown),
- a step d2) of separation carried out at high pressure and low temperature (CHPS) and fed with the gaseous effluent 21 and the other part of the liquid effluent 22b obtained from step d1) and an aqueous solution 12 and making it possible to obtain at least one second gaseous effluent 13 comprising hydrogen, an aqueous effluent 14 containing dissolved salts and dissolved H_2S and NH_3 , and a washed hydrocarbon effluent 23;
- a hydrotreatment step c) fed with the washed hydrocarbon effluent 23 freed in particular of chlorine impurities and obtained from separation step d) and with a stream of a hydrogen-rich gas 8, in order to obtain a hydrotreated hydrocarbon effluent 15.

Optionally, a step e) of fractionation of the hydrotreated hydrocarbon effluent 15 is carried out, making it possible to obtain at least one gaseous effluent 16, a naphtha cut 17 and a middle distillates cut 18.

On conclusion of step e), a part of the naphtha cut 17 can be sent to a steam cracking process (not illustrated). Another part of naphtha cut 17 can feed selective hydrogenation step a), hydrogenation step b) and/or hydrotreatment step c) (recycling not illustrated).

In Figure 4, at least a part of middle distillates cut 18 obtained from step e) feeds a hydrocracking step f) which is carried out in at least one fixed-bed reactor comprising at least one hydrocracking catalyst and is fed with hydrogen 19. The hydrocracked effluent 20 can be recycled between separation steps d1) and d2) or also upstream of separation step d) (not illustrated).

Only the main steps, with the main streams, are represented in Figures 1 to 4, in order to enable a better understanding of the invention. It is clearly understood that all the items of equipment required for the operation are present (drums, pumps, exchangers, ovens/furnaces, columns, and the like), even if not represented. It is also understood that (supply or recycle) hydrogen-rich gas streams, as described above, can be injected at the

inlet of each reactor or catalytic bed or between two reactors or two catalytic beds. Means well known to those skilled in the art for the purification and recycling of hydrogen can also be employed.

EXAMPLES

Example 1 (in accordance with the invention)

The feedstock treated in the process with a flow rate of 10 000 kg/h (10 T/h) is a tyre pyrolysis oil (that is to say, comprising 100% by weight of said tyre pyrolysis oil) having the characteristics indicated in Table 2.

Table 2: Characteristics of the feedstock

Property	Method	Unit	Tyre Pyrolysis Oil
Density at 15°C	NF EN ISO 12185	g/cm ³	0.907
Bromine Number	ASTM D1159	g/100 g	73
MAV	IFPEN 9407	mg/g	34
S	ASTM D5453	mg/kg	4892
N	ASTM D4629	mg/kg	2720
Cl	ASTM D7536	mg/kg	6
Si	ASTM D5185	mg/kg	10
Simulated Distillation	ASTM D2887		
Initial Boiling Point (0.50%)		°C	87
10%		°C	173
30%		°C	243
50%		°C	302
70%		°C	363
90%		°C	440
Final Boiling Point (99.50%)		°C	551

The feedstock is mixed with a liquid recycle, that is to say a part of the liquid effluent obtained from a hot drum of separation step d), in the proportions of 80/20 by mass, i.e. 40 T/h of liquid recycle per 10 T/h of feedstock. The mixture obtained is subjected to a hydrogenation step b) carried out in a fixed-bed reactor and in the presence of hydrogen and of a NiMo-on-alumina-type hydrogenation catalyst, under the conditions indicated in Table 3.

Table 3: Conditions of hydrogenation step b)

Reactor inlet temperature	°C	290
Reactor outlet temperature	°C	320
Average temperature (WABT)	°C	305
Hydrogen partial pressure	MPa abs.	5.7
H ₂ /HC (hydrogen coverage by volume, relative to the volume of feedstock)	Sm ³ /m ³	300
HSV (flow rate by volume of (fresh) feedstock/volume of catalysts)	h ⁻¹	0.8

The conditions indicated in Table 3 correspond to conditions at the start of the cycle.

On conclusion of the hydrogenation step b), the degrees of conversion (= (initial concentration - final concentration) / initial concentration) observed are indicated in Table 4.

Table 4: Conversions of the species during hydrogenation step b)

Degree of conversion of the diolefins	%	> 80
Degree of conversion of the olefins	%	> 70
Retention of silicon	%	> 85

The effluent obtained from hydrogenation step b) is subjected directly, without separation, to a hydrotreatment step b) carried out in a fixed bed and in the presence of hydrogen and of a NiMo-on-alumina-type hydrotreatment catalyst, under the conditions presented in Table 5.

Table 5: Conditions of hydrotreatment step c)

Average temperature of hydrotreatment (WABT)	°C	325
Hydrogen partial pressure	MPa abs.	5.5
Hydrogen sulfide partial pressure	MPa abs.	0.019
H ₂ /HC (hydrogen coverage by volume, relative to the volume of feedstock)	Sm ³ /m ³	400
HSV (flow rate by volume of feedstock/volume of catalysts)	h ⁻¹	0.5

The conditions indicated in Table 5 correspond to conditions at the start of the cycle.

The effluent obtained from hydrotreatment step c) is subjected to a separation step d) comprising a separation step d1) and a separation step d2). The effluent obtained from hydrotreatment step c) is subject to separation step d1) comprising a high-pressure separator drum operated at 300°C and 5.2 MPa abs. The fraction obtained at the bottom of the high-pressure hot drum makes it possible, via a pump, to recycle a part of the effluent to the inlet of hydrogenation step b). The fraction obtained at the top of the high-pressure hot drum is mixed with the part obtained at the bottom of the high-pressure hot drum that is not recycled to the inlet of hydrogenation step b). This hydrocarbon mixture is subjected to separation step d2) in which a stream of water is injected. The hydrocarbon mixture and the stream of water are then treated in an acid gas washing column and separator drums in order to obtain a gas fraction, an aqueous effluent comprising salts and a liquid effluent. The yields and quality of the various fractions obtained after separation are indicated in Table 6 (the yields correspond to the ratios of the amounts by mass of the various products obtained, relative to the mass of feedstock upstream of step b), expressed as a percentage and denoted % m/m).

Table 6: Yields and quality of the various products obtained after separation

Gas fraction yield ($\text{NH}_3 + \text{H}_2\text{S} + \text{C1-C4}$)	% m/m	1.43
Liquid fraction yield	% m/m	100.12
Nitrogen content of the liquid fraction (ASTM D4629)	mg/kg	7
Sulfur content of the liquid fraction (ASTM D5453)	mg/kg	33
Chlorine content of the liquid fraction (ASTM D7536)	mg/kg	3
Silicon content of the liquid fraction (ASTM D5185)	mg/kg	< 1

All or part of the liquid fraction obtained can subsequently be upgraded in a steam cracking step for the purpose of forming olefins which can be polymerized for the purpose of forming recycled plastics.

The tyre pyrolysis oil feedstock contains lots of sulfur (4892 ppm by weight). This sulfur which is present in the form of sulfur-containing molecules is hydrogenated in the reaction section and is converted to hydrogen sulfide H_2S . This H_2S , in the form of H_2S partial pressure (H_2Spp) of 0.019 MPa abs. at the outlet of the hydrotreatment reactor, contributes to maintaining the sulfide phase of the NiMo-on-alumina catalysts and hence to the activity of the catalyst. Consequently, the loss of catalytic activity of hydrotreatment step c) is low (< 1°C month) and it is not necessary to inject hydrogen sulfide or a sulfur compound such as DMDS in order to maintain the catalytic activity.

Example 2 (in accordance with the invention)

The feedstock treated in the process with a flow rate of 10 000 kg/h (10 T/h) is a 6/94 m/m mixture of the tyre pyrolysis oil of example 1 and of plastics pyrolysis oil (that is to say, comprising 6% by weight of said tyre pyrolysis oil and 94% by weight of said plastics pyrolysis oil) having the characteristics indicated in Table 7.

Table 7: Characteristics of the feedstock

Property	Method	Unit	6/94 m/m mixture of tyre pyrolysis oil and plastics pyrolysis oil
Density at 15°C	NF EN ISO 12185	g/cm ³	0.804
Bromine Number	ASTM D1159	g/100 g	50
MAV	IFPEN 9407	mg/g	12
S	ASTM D5453	mg/kg	355
N	ASTM D4629	mg/kg	965
Cl	ASTM D7536	mg/kg	88
Si	ASTM D5185	mg/kg	19
Simulated Distillation	ASTM D2887		
Initial Boiling Point (0.50%)		°C	60
10%		°C	134
30%		°C	198
50%		°C	267
70%		°C	330
90%		°C	397
Final Boiling Point (99.50%)		°C	561

The feedstock is mixed with a liquid recycle, that is to say a part of the liquid effluent obtained from a hot drum of separation step d), in the proportions of 80/20 by mass, i.e. 40 T/h of liquid recycle per 10 T/h of feedstock. The mixture obtained is subjected to a hydrogenation step b) carried out in a fixed-bed reactor and in the presence of hydrogen and of a NiMo-on-alumina-type hydrogenation catalyst, under the conditions indicated in Table 8.

Table 8: Conditions of hydrogenation step b)

Reactor inlet temperature	°C	290
Reactor outlet temperature	°C	320
Average temperature (WABT)	°C	305
Hydrogen partial pressure	MPa abs.	5.7
H ₂ /HC (hydrogen coverage by volume, relative to the volume of feedstock)	Sm ³ /m ³	300
HSV (flow rate by volume of feedstock/volume of catalysts)	h ⁻¹	0.8

The conditions indicated in Table 8 correspond to conditions at the start of the cycle.

On conclusion of the hydrogenation step b), the degrees of conversion (= (initial concentration - final concentration) / initial concentration) observed are indicated in Table 9.

Table 9: Conversions of the species during hydrogenation step b)

Degree of conversion of the diolefins	%	> 85
Degree of conversion of the olefins	%	> 75
Retention of silicon	%	> 90

The effluent obtained from hydrogenation step b) is subjected directly, without separation, to a hydrotreatment step b) carried out in a fixed bed and in the presence of hydrogen and of a NiMo-on-alumina-type hydrotreatment catalyst, under the conditions presented in Table 10.

Table 10: Conditions of hydrotreatment step c)

Average temperature of hydrotreatment (WABT)	°C	325
Hydrogen partial pressure	MPa abs.	5.5
Hydrogen sulfide partial pressure	MPa abs.	0.0027
H ₂ /HC (hydrogen coverage by volume, relative to the volume of feedstock)	Sm ³ /m ³	400
HSV (flow rate by volume of feedstock/volume of catalysts)	h ⁻¹	0.5

The conditions indicated in Table 10 correspond to conditions at the start of the cycle.

The effluent obtained from hydrotreatment step c) is subjected to a separation step d) comprising a separation step d1) and a separation step d2). The effluent obtained from hydrotreatment step c) is subject to separation step d1) comprising a high-pressure separator drum operated at 300°C and 5.2 MPa abs. The fraction obtained at the bottom of the high-pressure hot drum makes it possible, via a pump, to recycle a part of the effluent to the inlet of hydrogenation step b). The fraction obtained at the top of the high-pressure hot drum is mixed with the part obtained at the bottom of the high-pressure hot drum that is not recycled to the inlet of hydrogenation step b). This hydrocarbon mixture is subjected to separation step d2) in which a stream of water is injected. The hydrocarbon mixture and the stream of water are then treated in an acid gas washing column and separator drums in order to obtain a gas fraction, an aqueous effluent comprising salts and a liquid effluent. The yields and quality of the various fractions obtained after separation are indicated in Table 11 (the yields correspond to the ratios of the amounts by mass of the various products obtained, relative to the mass of feedstock upstream of the step b), expressed as a percentage and denoted % m/m).

Table 11: Yields and quality of the various products obtained after separation

Gas fraction yield ($\text{NH}_3 + \text{H}_2\text{S} + \text{C1-C4}$)	% m/m	1.19
Liquid fraction yield	% m/m	99.87
Nitrogen content of the liquid fraction (ASTM D4629)	mg/kg	3
Sulfur content of the liquid fraction (ASTM D5453)	mg/kg	8
Chlorine content of the liquid fraction (ASTM D7536)	mg/kg	2
Silicon content of the liquid fraction (ASTM D5185)	mg/kg	< 1

All or part of the liquid fraction obtained can subsequently be upgraded in a steam cracking step for the purpose of forming olefins which can be polymerized for the purpose of forming recycled plastics.

The feedstock consisting of the mixture of plastics pyrolysis oil and tyre pyrolysis oils has a significant content of sulfur (355 ppm by weight). This sulfur which is present in the form of sulfur-containing molecules is hydrogenated in the reaction section and is converted to hydrogen sulfide H_2S . This H_2S , in the form of H_2S partial pressure (H_2Spp) of

0.0027 MPa abs. at the outlet of the hydrotreatment reactor, contributes to maintaining the sulfide phase of the NiMo-on-alumina catalysts and hence to the activity of the catalyst. Consequently, the loss of catalytic activity of hydrotreatment step c) is low ($< 1^{\circ}\text{C}$ month) and it is not necessary to inject hydrogen sulfide or a sulfur compound such as DMDS in order to maintain the catalytic activity.

Example 3 (not in accordance with the invention)

According to Example 3, the feedstock treated is a plastics pyrolysis oil (i.e. comprising 100% by weight of said plastics pyrolysis oil) having the characteristics indicated in Table 12.

Table 12: Characteristics of the feedstock

Property	Method	Unit	Plastics Pyrolysis Oil
Density at 15°C	NF EN ISO 12185	g/cm ³	0.798
Bromine Number	ASTM D1159	g/100 g	50
MAV	IFPEN 9407	mg/g	11
S	ASTM D5453	mg/kg	67
N	ASTM D4629	mg/kg	871
Cl	ASTM D7536	mg/kg	95
Si	ASTM D5185	mg/kg	20
Simulated Distillation	ASTM D2887		
Initial Boiling Point (0.50%)		°C	60
10%		°C	134
30%		°C	199
50%		°C	270
70%		°C	335
90%		°C	403
Final Boiling Point (99.50%)		°C	574

The plastics pyrolysis oil according to Example 3 is treated under the same conditions as the tyre pyrolysis oil according to Example 1.

The plastics pyrolysis oil feedstock contains very little sulfur (67 ppm by weight). This sulfur which is present in the form of sulfur-containing molecules is hydrogenated in the reaction

section and is converted to H_2S . This H_2S , in the form of H_2S partial pressure (H_2Spp) of 0.0004 MPa abs. at the outlet of the hydrotreatment reactor, contributes partially to maintaining the sulfide phase of the NiMo-on-alumina catalysts. Nevertheless, the H_2Spp obtained with this content of sulfur in the feedstock (67 ppm by weight) is insufficient to maintain the catalysts in the sulfide phase throughout the cycle. This results in a rapid deactivation of the activity of the catalyst.

Example 4 (not in accordance with the invention)

According to Example 4, the feedstock treated is identical to the plastics pyrolysis oil treated in Example 3. The feedstock according to Example 4 is treated under the same conditions as in Example 3, but the H_2S is added to the reaction system in order to achieve a sufficient H_2Spp . This addition of H_2S can be carried out in the form of an injection, at the inlet of the unit, into the pyrolysis oil feedstock, of dimethyl disulfide (DMDS). DMDS readily decomposes as soon as it contacts the catalyst to give CH_4 and H_2S , thus generating a sufficient H_2Spp to maintain the catalysts in sulfide form. This way of operating causes a high consumption of DMDS harmful to the economics of the process.

Taking the sulfur content of the feedstock into account, DMDS is injected at a content of 800 ppm (content equivalent to 544 ppm by weight of sulfur) so as to achieve the same hydrogen sulfide partial pressure as that obtained in Example 2, i.e. 0.0027 MPa abs. For a capacity of 10 T/h of treated feedstock, this represents a consumption of DMDS of 8.0 kg/h and thus a significant operating and environmental cost.

Example 5 (not in accordance with the invention)

According to Example 5, the feedstock treated is identical to the plastics pyrolysis oil treated in Example 3, except for having a very high content of chlorine (2000 ppm by weight) and a nitrogen content of 700 ppm by weight. The plastics pyrolysis oil according to Example 5 is treated under the same conditions as the tyre pyrolysis oil according to Example 3. An injection of 16.5 kg/h of aniline is necessary in order to scavenge all of the Cl ions.

Example 6 (in accordance with the invention)

According to Example 6, the feedstock treated is a mixture comprising 15% by weight of tyre pyrolysis oil of Example 1 (with a content of 2720 ppm by weight of nitrogen) and 85% by weight of plastics pyrolysis oil of Example 5 (with a content of 2000 ppm by weight of sulfur and 700 ppm by weight of nitrogen). The feedstock according to Example 6 is treated under the same conditions as the feedstock (100% by weight of plastics oil) according to Example 5. It is not necessary to inject an amine since the tyre pyrolysis oil provides the nitrogen

necessary to scavenge all of the Cl ions. In addition, it is not necessary to inject hydrogen sulfide or a sulfur compound such as DMDS in order to maintain the catalytic activity.

CLAIMS

1. Process for treating a feedstock comprising at least 5% by weight of a tyre pyrolysis oil relative to the total weight of the feedstock, said tyre pyrolysis oil having a sulfur content of between 2000 and 10 000 ppm by weight relative to the total weight of the oil, said process comprising the following steps:

a) optionally a selective hydrogenation step carried out in a reaction section employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one selective hydrogenation catalyst, said selective hydrogenation reaction section being fed at least with said feedstock and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at an average temperature between 100 and 280°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 selectively hydrogenated effluent,

b) a hydrogenation step carried out in a hydrogenation reaction section, employing at least one fixed-bed reactor having n catalytic 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 feedstock or said selectively hydrogenated effluent obtained from step a) and a gas stream comprising hydrogen, said hydrogenation reaction section being implemented at an average temperature between 140 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 hydrogenated effluent,

c) a hydrotreatment step carried out in a hydrotreatment reaction section, employing at least one fixed-bed reactor having n catalytic beds, n being an integer greater than or equal to 1, each comprising at least one hydrotreatment catalyst, said hydrotreatment reaction section being fed at least with said hydrocarbon effluent obtained from step d) when separation step d) is carried out between steps b) and c), and/or at least with the hydrogenated effluent obtained from step b) when separation step d) is carried out after step c), and a gas stream comprising hydrogen, said hydrotreatment reaction section being implemented at an average temperature between 250 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 effluent,

d) a separation step, carried out between steps b) and c) and/or after step c), said step being fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c)

when separation step d) is carried out after step c), and an aqueous solution, said step being performed in a separation section, in order to obtain at least one gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

2. Process according to Claim 1, wherein the feedstock comprises a plastics and/or solid recovered fuels pyrolysis oil.

3. Process according to either of the preceding claims, wherein the feedstock consists of a tyre pyrolysis oil and of plastics and/or solid recovered fuels pyrolysis oil(s).

4. Process according to one of the preceding claims, wherein the feedstock comprises a tyre pyrolysis oil in a content of between 5% and 99% by weight and a plastics and/or solid recovered fuels pyrolysis oil in a content of between 1% and 95% by weight relative to the total weight of the feedstock.

5. Process according to one of the preceding claims, wherein the separation step d) comprises the following steps:

d1) a separation step, fed with the hydrogenated effluent obtained from step b) when separation step d) is carried out between steps b) and c), and/or with the hydrotreated effluent obtained from step c) when separation step d) is carried out after step c), said step being performed at a temperature greater than the precipitation temperature of the ammonium halides and at a pressure substantially identical to the pressure of step b) in order to obtain at least one first gaseous effluent and a liquid effluent of which a part is optionally recycled, as recycled effluent, upstream of step b),

d2) a separation step, fed with the first gaseous effluent and optionally at least a part of the liquid effluent obtained from step d1), and an aqueous solution, said step being performed at a temperature lower than the precipitation temperature of the ammonium halides and at a pressure substantially identical to or lower than the pressure of step b), in order to obtain at least one second gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

6. Process according to the preceding claim, wherein step d1) is performed at a temperature of between 200 and 450°C and step d2) is performed at a temperature of greater than or equal to 20°C and less than 200°C.

7. Process according to one of the preceding claims, comprising at least one step of pretreating the feedstock comprising a tyre pyrolysis oil, said pretreatment step being carried out upstream of step a) and/or upstream of step b), and comprises an adsorption step and/or a filtration step and/or a centrifugation step and/or a settling 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, comprising a step e) of fractionating all or part of the hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or all or part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), in order to obtain at least one gas stream, a naphtha cut and at least one middle distillates cut.

9. Process according to one of the preceding claims, comprising at least one hydrocracking step f) carried out in a hydrocracking reaction section, employing at least one fixed-bed reactor having n catalytic 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 at least a part of said hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or with at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c), and/or else with at least a part of the middle distillates cut obtained from fractionation step e) and a gas stream comprising hydrogen, said hydrocracking reaction section being implemented at an average temperature between 250 and 450°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 first hydrocracked effluent.

10. Process according to one of the preceding claims, wherein said hydrogenation catalyst of step b) comprises a support chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof and a hydro-dehydrogenating function comprising either at least one element from group VIII and at least one element from group VIB, or at least one element from group VIII.

11. Process according to one of the preceding claims, wherein said hydrotreatment catalyst of step c) comprises a support chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof, and a hydro-dehydrogenating function comprising at least one element from group VIII and/or at least one element from group VIB.

12. Process according to one of the preceding claims, wherein at least a part of the hydrocarbon effluent obtained from step d) when separation step d) is carried out after step c), and/or at least a part of the hydrotreated effluent obtained from step c) when separation step d) is carried out between steps b) and c) and/or else at least one of the cuts obtained from fractionation step e) is sent to a steam cracking step g) carried out in at least one pyrolysis furnace at a temperature of between 700 and 900°C and at a pressure of between 0.05 and 0.3 MPa relative.

13. Process according to one of the preceding claims, comprising selective hydrogenation step a).

14. Process according to the preceding claim, wherein said selective hydrogenation catalyst of step a) comprises a support chosen from alumina, silica, silica-aluminas, magnesia, clays and mixtures thereof, and a hydro-dehydrogenating function comprising at least one element from group VIII and/or at least one element from group VIB.

15. Product obtained by the process according to one of Claims 1 to 14.

16. Product according to Claim 15, which comprises, relative to the total weight of the product:

- a total content of metal elements of less than or equal to 10.0 ppm by weight,
- including a content of iron element of less than or equal to 200 ppb by weight, and/or
- a content of silicon element of less than or equal to 5.0 ppm by weight, and/or
- a sulfur content of less than or equal to 100 ppm by weight, and/or
- a nitrogen content of less than or equal to 100 ppm by weight, and/or
- a content of chlorine element of less than or equal to 10 ppm by weight, and/or
- a mercury content of less than or equal to 5 ppb by weight.

17. Product according to Claims 15 and 16, comprising a content of biological carbon according to ASTM D6866 of between 1% and 70% by weight.