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(54) **Title:** METHOD FOR TREATING PLASTIC PYROLYSIS OIL INCLUDING AN H_2S RECYCLING STEP

(54) **Titre :** PROCEDE DE TRAITEMENT D'HUILE DE PYROLYSE DE PLASTIQUES INCLUANT UNE ETAPE DE RECYCLAGE D'H_2S

(57) **Abstract:** The present invention relates to a method for treating a plastic pyrolysis oil, the method comprising: - hydrotreating the feedstock in the presence of hydrogen and a catalyst; - separating/washing the hydrotreated effluent in the presence of an aqueous solution to obtain at least a first aqueous effluent and a hydrotreated hydrocarbon effluent; - separating the H_2S contained in the first aqueous effluent to obtain a gas phase containing the H_2S and a second aqueous effluent, the gas phase containing the H_2S can be at least partially recycled upstream of step b); - separating the NH_3 contained in the second aqueous effluent to obtain a gas phase containing NH_3 and a third aqueous effluent. The present invention makes it possible, by recycling the H_2S coming from the method, to decrease the consumption of the sulphurising agent to maintain the catalysts in sulphide form in feedstocks having low sulphur content.

(57) **Abrégé :** La présente invention concerne un procédé de traitement d'une huile de pyrolyse de plastiques, comprenant : - un hydrotraitement de la charge en présence d'hydrogène et d'un catalyseur; - une séparation/lavage de l'effluent hydrotraité en présence d'une solution aqueuse pour obtenir au moins un premier effluent aqueux et un effluent hydrocarboné hydrotraité - une séparation de l'H_2S contenu dans le premier effluent aqueux pour obtenir une phase gazeuse contenant l'H_2S et un deuxième effluent aqueux, ladite phase gazeuse contenant l'H_2S peut au moins en partie être recyclée en amont de l'étape b), - une séparation du NH_3 contenu dans le deuxième effluent aqueux pour obtenir une phase gazeuse contenant du NH_3 et un troisième effluent aqueux. La présente invention permet par le recyclage de l'H_2S issu du procédé de diminuer la consommation d'agent sulfurant pour maintenir les catalyseurs sous forme sulfures dans des charges contenant que peu de soufre.

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METHOD FOR TREATING PLASTIC PYROLYSIS OIL INCLUDING AN H_2S RECYCLING STEP

TECHNICAL FIELD

The present invention relates to a process for the treatment of a plastics pyrolysis oil in order to obtain a hydrocarbon effluent which can be upgraded in a unit for the storage of petrol, jet or gas-oil fuels or as feedstock of a steam cracking unit. More particularly, the present invention relates to a process for the treatment of a feedstock resulting from the pyrolysis of plastic waste making it possible to recycle a gas phase containing H_2S resulting from the process in order to keep the catalysts in sulfide form in the catalytic stages of the process and thus to reduce the consumption of sulfiding agent to be added.

PRIOR ART

Plastics resulting from collection and sorting channels can undergo a stage of pyrolysis in order to obtain, *inter alia*, pyrolysis oils. These plastics pyrolysis oils are generally incinerated in order to generate electricity and/or used as fuel in industrial or urban heating boilers.

Another route for upgrading plastics pyrolysis oils is the use of these plastics pyrolysis oils as feedstock of a steam cracking unit in order to (re)create olefins, the latter being constituent monomers of certain polymers. However, plastic waste is generally a mixture of several polymers, for example mixtures of polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride or polystyrene. Furthermore, depending on the applications, the plastics may contain, in addition to polymers, other compounds, such as plasticizers, pigments, dyes or also residues of polymerization catalysts. Plastic waste may additionally contain, in a minor amount, biomass originating, for example, from household waste. The treatment of waste, on the one hand, in particular the storage, mechanical treatments, sorting or pyrolysis, and also, on the other hand, the storage and transportation of pyrolysis oil, can also cause corrosion. The result of this is that the oils resulting from the pyrolysis of plastic waste comprise a lot of impurities, in particular diolefins, metals, in particular iron, silicon, or also halogen compounds, in particular chlorine-based compounds, heteroelements, such as sulfur, oxygen and nitrogen, and insoluble materials, at contents which are often high and incompatible 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, coking or catalytic deactivation, or also incompatibility problems in the applications of the

target polymers. The presence of diolefins can also result in problems of instability of the pyrolysis oil, characterized by the formation of gums. The gums and the insoluble materials possibly present in the pyrolysis oil can give rise to problems of clogging in the processes.

Furthermore, during the steam cracking stage, the yields of light olefins sought for the petrochemical industry, in particular ethylene and propylene, are strongly dependent on the quality of the feedstocks sent for steam cracking. The BMCI (Bureau of Mines Correlation Index) is often used to characterize hydrocarbon cuts. This index, developed for hydrocarbon products resulting from crude oils, is calculated from the measurement of the density and the average boiling point: it is equal to 0 for a linear paraffin and to 100 for benzene. Its value thus increases in proportion as the product analysed has a condensed aromatic structure, naphthenes having a BMCI intermediate between paraffins and aromatics. Overall, the yields of light olefins increase when the paraffin content increases and thus when the BMCI decreases. Conversely, the yields of undesired heavy compounds and/or of coke increase when the BMCI increases.

The document WO 2018/055555 provides an overall process for the recycling of plastic waste, which is very general and relatively complex, ranging from the very stage of pyrolysis of the plastic waste up to the steam cracking stage. The process of the application WO 2018/055555 comprises, *inter alia*, a stage of hydrotreating the liquid phase resulting directly from the pyrolysis, preferably under quite stringent conditions, in particular in terms of temperature, for example at a temperature of between 260 and 300°C, a stage of separation of the hydrotreating effluent and then a stage of hydrodealkylation of the separated heavy effluent at a preferably high temperature, for example of between 260 and 400°C.

The unpublished patent application FR 21/00.026 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 stages:

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 stage a) being at least 15°C greater than the inlet temperature of stage a), in order to obtain a hydrogenated effluent;

b) the hydrotreating of said hydrogenated effluent in the presence at least of hydrogen and of at least one hydrotreating catalyst, in order to obtain a hydrotreated effluent, the average temperature of stage b) being greater than the average temperature of stage 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 a gaseous effluent, an aqueous liquid effluent and a hydrocarbon liquid effluent.

One route for removing the impurities contained in the ex-plastics pyrolysis oils is thus to carry out a hydrotreating 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. In point of fact, a minimum pH_2Sp is necessary in the hydrotreating reactor in order to keep the catalysts in sulfide form and thus not to reduce them. In order to maintain a sufficient pH_2Sp in the reactor and in view of the fact that the 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 pH_2Sp.

After the hydrotreating, at least a portion of the H_2S contained in the effluent forms ammonium sulfide salts ($(NH_4)_2S$) with the NH_3 generated by the hydrogenation of nitrogen compounds during the hydrotreating. Unlike conventional feedstocks of fossil type, ex-plastics pyrolysis oils generally contain greater contents of nitrogen than contents of sulfur. These salts are generally removed by scrubbing with water, followed by a (single) stage of steam stripping of the aqueous effluent, making it possible to obtain a purified aqueous effluent and a gas phase containing H_2S and NH_3, which are generally discharged together at the top of the stripping column. The gas phase containing H_2S and NH_3 is subsequently generally incinerated to form SO_x (sulfur oxides) and N_2 or NO_x (nitrogen oxides).

The gas phase containing H_2S and NH_3 might be recovered and returned to the inlet of the hydrotreating unit in order to maintain the pH_2Sp in the reactor without adding a sulfiding agent. However, the NH_3 contained in this gas phase prevents this from being done as there would be a concentration of NH_3 in the recycling loop which would be prejudicial to the operation of the unit. Furthermore, the presence of NH_3 lowers the pH_2p. The gas phase containing H_2S and NH_3 thus cannot be reused directly as source of H_2S for keeping the catalysts in sulfide form.

The present invention provides a process for the treatment of a feedstock comprising a plastics pyrolysis oil which makes possible the recycling of a phase containing only H_2S in order to use it as source of H_2S at the inlet of catalytic units of the process by carrying out a

separation, generally by stripping, in two stages, making it possible to separate the H_2S and the NH_3. This is because the use of two stripping columns operating under different operating conditions makes it possible to separate the H_2S from the NH_3 and thus to recover:

- a gas phase containing the H_2S which can be recycled at the inlet of the hydrotreating unit;
- and a gas phase containing the NH_3 which can be incinerated or also be recycled at the inlet of the hydrotreating unit.

The two-stage stripping making it possible to separate the H_2S from the NH_3 thus exhibits the following advantages:

- the removal of the NH_3 from the phase containing only the H_2S makes possible the recycling of the H_2S at the inlet of the catalytic units of the process;

- high minimization of the consumption of sulfiding agent;

- the elimination of the gas phase containing the NH_3 by incinerating it is easier as it no longer contains the H_2S forming pollutants of SO_x type;

- the gas phase containing the NH_3 can also be recycled at the inlet of the catalytic units, advantageously in stoichiometric amounts suitable for the formation of the salts during the separation/scrubbing stage c);

- better observation of environmental constraints as regards SO_x as the majority of the H_2S is not incinerated (but, on the contrary, recycled in a loop);

- a fall in the consumption of hydrogen in the hydrotreating unit because the sulfiding agent (DMDS) consumes hydrogen in order to break down;

- complete removal of the NH_3 in the gaseous effluent comprising hydrogen and/or light hydrocarbons from the top of the separation/scrubbing section (stage c) described below). This is because the NH_3 has been captured in the form of ammonium sulfide in the aqueous effluent by the excess H_2S which has been recycled. The gaseous effluent, thus freed from the NH_3, can thus be sent to a steam cracker so as to increase the overall yield of olefins.

SUMMARY OF THE INVENTION

More specifically, the invention relates to a process for the treatment of a feedstock comprising a plastics pyrolysis oil, comprising:

a) optionally a hydrogenation stage 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 and a gas stream comprising hydrogen, said hydrogenation reaction section being employed 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,

b) a hydrotreating stage carried out in a hydrotreating reaction section comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with the feedstock or said hydrogenated effluent resulting from stage a) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed 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,

c) a separation stage, fed with the hydrotreated effluent resulting from stage b) and optionally with the hydrocracked effluent resulting from stage g) and an aqueous solution, in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent,

d) a stage of separation of the H_2S contained in the first aqueous effluent, in order to obtain a gas phase containing the H_2S and a second aqueous effluent, said gas phase containing the H_2S being optionally, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g),

e) a stage of separation of the NH_3 contained in the second aqueous effluent, in order to obtain a gas phase containing NH_3 and a third aqueous effluent, said gas phase containing NH_3 being optionally, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g),

f) optionally a stage of fractionation of all or part of the hydrocarbon effluent resulting from stage c), in order to obtain at least a gaseous effluent and at least a first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C and a second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C,

g) optionally, a hydrocracking stage 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 resulting from stage c) and/or with at least a part of the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C resulting from stage f) and a gas stream

comprising hydrogen, said hydrocracking reaction section being employed 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.

The present invention thus relates to a process making it possible to purify an oil resulting from the pyrolysis of plastic waste of at least a 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 recycle the H_2S resulting from the process continuously in order to minimize the consumption of sulfiding agent. The injection of a sulfiding agent remains in particular necessary at the start of the catalytic cycle, the time that the H_2S is formed in order to be separated in stage d) and recycled upstream of stage a) and/or of stage b) and/or of stage g), and/or also upstream of the selective hydrogenation stage a0). Additional injections throughout the catalytic cycle may be necessary in order to compensate for the natural loss. However, the fact of being able to recycle a gas phase containing the H_2S without the NH_3 by the present invention makes it possible to considerably reduce the consumption of the sulfiding agent.

Another advantage is the removal of the NH_3 in the gaseous effluent comprising hydrogen and/or light hydrocarbons from the top of the separation/scrubbing section (stage c)) by reaction with the recycled excess H_2S in the form of ammonium sulfide in the aqueous effluent. In other words, the NH_3 leaves in the form of salt in the aqueous effluent.

Another advantage of the invention is that of preventing risks of plugging and/or of corrosion of the treatment unit in which the process of the invention is carried out, the risks being exacerbated by the presence, often in large amounts, of diolefins, metals and halogen compounds in the plastics pyrolysis oil.

The process of the invention thus makes it possible to obtain a hydrocarbon effluent, resulting from a plastics pyrolysis oil, which is freed, at least partly, of the impurities of the starting plastics pyrolysis oil, thus limiting the problems of operability, such as the corrosion, coking or catalytic deactivation problems, which may be brought about by these impurities, in particular in steam cracking units and/or in units located downstream of the steam cracking units, in particular the polymerization and hydrogenation units. The removal of at least a part of the impurities of the oils resulting from the pyrolysis of plastic waste will also make it

possible to increase the range of applications of the target polymers, the incompatibilities of usages being reduced.

According to an alternative form, said gas phase containing the H_2S resulting from stage d) is at least partly recycled upstream of stage a) and/or stage b) and/or stage g).

According to an alternative form, the process comprises the hydrogenation stage a).

According to an alternative form, the process comprises the fractionation stage f).

According to an alternative form, the process comprises the hydrocracking stage g).

According to an alternative form, stage d) of separation of the H_2S contained in the first aqueous effluent is carried out by stripping said effluent with a stream containing steam at a pressure of between 0.5 and 1 MPa and a temperature of between 80 and 150°C.

According to an alternative form, stage e) of separation of the NH_3 contained in the second aqueous effluent is carried out by stripping said effluent with a stream containing steam at a pressure of between 0.1 and 0.5 MPa and a temperature of between 80 and 150°C.

According to an alternative form, the separation stage c) comprises the following stages:

c1) a separation stage, fed with the hydrotreated effluent resulting from stage b), said stage being carried out at a temperature of between 200 and 450°C and at a pressure substantially identical to the pressure of stage b), in order to obtain at least a gaseous effluent and a liquid effluent, a part of which is optionally recycled upstream of stage a) and/or of stage b),

c2) a separation stage, fed with the gaseous effluent resulting from stage c1) and another part of the liquid effluent resulting from stage c1) and an aqueous solution, said stage being carried out at a temperature of between 20 and less than 200°C and at a pressure substantially identical to or less than the pressure of stage b), in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent.

According to an alternative form, the process comprises at least one stage a0) of pretreatment of the feedstock comprising a plastics pyrolysis oil, optionally as a mixture with the hydrocarbon effluent resulting from stage c), said pretreatment stage being carried out upstream of stage a) and/or upstream of stage b), and comprises a filtration stage and/or a centrifugation stage and/or an electrostatic separation stage and/or a stage of scrubbing by means of an aqueous solution and/or an adsorption stage and/or a selective hydrogenation stage.

According to an alternative form, the hydrocarbon effluent resulting from the separation stage c), or at least one of the two liquid hydrocarbon cuts resulting from stage f), is sent, completely or partly, to a steam cracking stage h) 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 an alternative form, said gas phase containing NH_3 resulting from stage e) is at least partly recycled upstream of stage a) and/or stage b) and/or stage g).

According to an alternative form, a stream containing a nitrogen compound and/or a sulfur compound is injected upstream of stage a) and/or upstream of stage b).

According to an alternative form, said hydrogenation catalyst comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and their mixtures 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 an alternative form, said hydrotreating catalyst comprises a support chosen from the group consisting of alumina, silica, silicas-aluminas, magnesia, clays and their mixtures and a hydro-dehydrogenating function comprising at least one element from group VIII and/or at least one element from group VIB.

According to an alternative form, the process additionally comprises a second hydrocracking stage g') 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 resulting from the first hydrocracking stage g) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed at a 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.

According to an alternative form, said hydrocracking catalyst comprises a support chosen from halogenated aluminas, combinations of boron and aluminium oxides, amorphous silica-aluminas and zeolites and a hydro-dehydrogenating function comprising at least one metal from group VIB chosen from chromium, molybdenum and tungsten, alone or as a mixture, and/or at least one metal from group VIII chosen from iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum.

The invention also relates to the product liable to be obtained, and preferably obtained, by the process according to the invention.

According to this alternative form, the product comprises, with respect 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 the present invention, the pressures are absolute pressures, also denoted abs., and are given in MPa absolute (or MPa abs.), unless otherwise indicated.

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 described range, such a piece of information will be revealed by the present invention.

Within the meaning of the present invention, the various parameter ranges for a given stage, such as the pressure ranges and the temperature ranges, can be used alone or in combination. For example, within the meaning of the present invention, a range of preferred pressure values can be combined with a range of more preferred temperature values.

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

Subsequently, the groups of chemical elements are given according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, editor-in-chief D.R.

Lide, 81st edition, 2000-2001). For example, group VIII (or VIIIB) according to the CAS classification corresponds to the metals of columns 8, 9 and 10 according to the new IUPAC classification.

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

DETAILED DESCRIPTION

The feedstock

According to the invention, a “plastics pyrolysis oil” is an oil, advantageously in liquid form at ambient temperature, resulting from the pyrolysis of plastics, preferably of plastic waste originating in particular from collection and sorting channels. It can also result from the pyrolysis of worn tyres.

It comprises in particular a mixture of hydrocarbon compounds, especially paraffins, mono- and/or diolefins, naphthenes and aromatics. At least 80% by weight of these hydrocarbon compounds preferably have a boiling point of less than 700°C and preferably of less than 550°C. In particular, depending on the origin of the pyrolysis oil, the latter can comprise up to 70% by weight of paraffins, up to 90% by weight of olefins and up to 90% by weight of aromatics, it being understood that the sum of the paraffins, of the olefins and of the aromatics is 100% by weight of the hydrocarbon compounds.

The density of the pyrolysis oil, measured at 15°C according to the ASTM D4052 method, is generally of between 0.75 and 0.99 g/cm^3, preferably of between 0.75 and 0.95 g/cm^3.

The plastics pyrolysis oil can additionally comprise, and usually does comprise, impurities such as metals, in particular iron, silicon or halogen compounds, in particular chlorine compounds. These impurities can be present in the plastics pyrolysis oil at high contents, for example up to 350 ppm by weight or also 700 ppm by weight, indeed even 1000 ppm by weight, of halogen elements (in particular chlorine) contributed by halogen compounds, and up to 100 ppm by weight, indeed even 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 possibly contained in the oils resulting from the pyrolysis of plastic waste comprise silicon, iron or both these elements. The plastics pyrolysis oil can also comprise other impurities, such as heteroelements contributed in particular by sulfur compounds, oxygen compounds and/or nitrogen compounds, at contents generally of less than 27 000 ppm by weight of

heteroelements and preferably of less than 15 500 ppm by weight of heteroelements. The sulfur compounds are generally present in a content of less than 2000 ppm by weight and preferably of less than 500 ppm by weight. 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. The nitrogen compounds are generally present in a content of less than 10 000 ppm by weight and preferably of less than 5000 ppm by weight. The plastics pyrolysis oil can also comprise other impurities, such as heavy metals, for example mercury, arsenic, zinc and lead, for example up to 100 ppb by weight or also 200 ppb by weight of mercury.

The feedstock of the process according to the invention comprises at least one plastics pyrolysis oil. Said feedstock can consist solely of plastics pyrolysis oil(s). Preferably, said feedstock comprises at least 50% by weight, preferably between 70% and 100% by weight, of plastics pyrolysis oil, with respect to the total weight of the feedstock, that is to say preferably between 50% and 100% by weight and in a preferred way between 70% and 100% by weight of plastics pyrolysis oil.

The feedstock of the process according to the invention can comprise, in addition to the plastics pyrolysis oil(s), a conventional petroleum feedstock or a feedstock resulting from the conversion of biomass which is then co-treated with the plastics 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 resulting from the conversion of biomass can advantageously be chosen from vegetable oils, oils from algae or algal oils, fish oils, waste food oils, and fats of vegetable or animal origin, or mixtures of such feedstocks. Said vegetable oils can advantageously be crude or refined, completely or partly, and result from plants chosen from rape, sunflower, soybean, palm, olive, coconut, copra, castor oil plant, cotton plant, peanut oil, linseed oil and sea kale oil, and all the oils resulting, for example, from sunflower or rape by genetic modification or hybridization, this list not being limiting. Said animal fats are advantageously chosen from blubber and fats composed of residues from the food industry or resulting from the catering industries. Frying oils, various animal oils, such as fish oils, tallow or lard, can also be used. The feedstock resulting from the conversion of biomass can also advantageously be chosen from methyl esters of fatty acids of vegetable and/or animal origin or also methyl esters of fatty acids of waste food vegetable oils.

The feedstock resulting 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 their by-products. The term “lignocellulosic biomass” denotes biomass derived from plants or from their by-products. The lignocellulosic biomass is composed of carbohydrate polymers (cellulose, hemicellulose) and of an aromatic polymer (lignin).

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

The plastics pyrolysis oil can result from a thermal or catalytic pyrolysis treatment or also be prepared by hydropyrolysis (pyrolysis in the presence of a catalyst and of hydrogen).

Pretreatment (optional)

Said feedstock comprising a plastics pyrolysis oil, optionally as a mixture with the hydrocarbon effluent from stage c), can advantageously be pretreated in at least one optional pretreatment stage a0), prior to the hydrogenation stage a) and/or the hydrotreating stage b), in order to obtain a pretreated feedstock which feeds stage a) and/or stage b).

According to an alternative form, this optional pretreatment stage a0) makes it possible to reduce the amount of contaminants and of solid particles, in particular the amount of iron and/or of silicon and/or of chlorine, possibly present in the feedstock comprising a plastics pyrolysis oil. This optional stage a0) makes possible in particular the removal of sediments which can be formed as a result of the unstable nature of the pyrolysis oils and/or of a problem of compatibility between two different feedstocks. Thus, an optional stage a0) of pretreatment of the feedstock comprising a plastics pyrolysis oil is advantageously carried out, especially when said feedstock comprises more than 10 ppm by weight, in particular more than 20 ppm by weight, more particularly more than 50 ppm by weight, of metal elements and/or of solid particles, and especially when said feedstock comprises more than 5 ppm by weight of silicon, more particularly more than 10 ppm by weight, indeed even more than 20 ppm by weight, of silicon. Likewise, an optional stage a0) of pretreatment of the feedstock comprising a plastics pyrolysis oil is advantageously carried out especially when said feedstock comprises more than 10 ppm by weight, in particular more than 20 ppm by weight, more particularly more than 50 ppm by weight, of chlorine.

Said optional pretreatment stage a0) 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 a filtration stage and/or a centrifugation stage and/or an electrostatic separation stage and/or a stage of scrubbing by means of an aqueous solution and/or an adsorption stage and/or a selective hydrogenation stage.

When the optional pretreatment stage a0) comprises a filtration stage and/or a centrifugation stage and/or an electrostatic separation stage and/or a stage of scrubbing by means of an aqueous solution and/or an adsorption stage, it 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 an alternative form, said optional pretreatment stage a0) is carried out in an adsorption section operated in the presence of at least one adsorbent, preferably of alumina type, having a specific surface of greater than or equal to 100 m^2/g, preferably of greater than or equal to 200 m^2/g. The specific surface of said at least one adsorbent is advantageously less than or equal to 600 m^2/g, in particular less than or equal to 400 m^2/g. The specific surface of the adsorbent is a surface area measured by the BET method, that is to say the specific surface determined by nitrogen adsorption in accordance with Standard ASTM D 3663-78 established from the Brunauer-Emmett-Teller method described in the periodical *The Journal of the American Chemical Society*, 60, 309 (1938).
Advantageously, said adsorbent comprises less than 1% by weight of metal elements and is preferably devoid of metal elements. The term “metal elements of the adsorbent” should be understood as meaning the elements of Columns 6 to 10 of the Periodic Table of the Elements (new IUPAC classification). The residence time of the feedstock in the adsorption section is generally of between 1 and 180 minutes.

Said adsorption section of the optional stage a0) comprises at least one adsorption column, preferably comprises at least two adsorption columns, preferentially between two and four adsorption columns, containing said adsorbent. 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. When the adsorbent of the on-line column is spent, this column is isolated, while the column in reserve is placed on-line, i.e. in operation. The spent adsorbent can subsequently be regenerated *in situ* and/or replaced with fresh adsorbent so that the column containing it can again be brought back on-line once the other column has been isolated.

Another operating mode is to have at least two columns operating in series. When the adsorbent of the column placed at the head is spent, this first column is isolated and the spent adsorbent is either regenerated *in situ* or replaced with fresh adsorbent. The column is subsequently brought back on-line in the last position, and so on. This operation is known as permutable mode, or according to the term PRS for Permutable Reactor System, or also “lead and lag”. The combination of at least two adsorption columns makes it possible to overcome the possible and potentially rapid poisoning and/or clogging of the adsorbent due to the combined action of the metal contaminants, of the diolefins, of the gums resulting from the diolefins and of the insoluble matter which may be present in the plastics pyrolysis oil to be treated. The reason for this is that the presence of at least two adsorption columns facilitates the replacement and/or the regeneration of the adsorbent, advantageously without shutdown of the pretreatment unit, indeed even of the process, thus making it possible to reduce the risks of clogging and thus to avoid shutdown of the unit because of clogging, to control the costs and to limit the consumption of adsorbent.

According to another alternative form, said optional pre-treatment stage a0) is carried out in a section for scrubbing with an aqueous solution, for example water, or an acidic or basic solution. This scrubbing section can contain 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 cocurrentwise or countercurrentwise scrubbing column.

According to another alternative form, said optional pretreatment stage a0) is carried out by filtration. The filtration stage 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, in an even more preferred way less than or equal to 5 µm. According to another alternative form, use may be made of a filter, the size of the pores of which is less than 25 µm but greater than 5 µm. Use may also be made of a series of filters with different pore sizes, in particular a series of filters having pore sizes decreasing 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. The solids content can be measured, for

example, by the Heptane Insolubles test, ASTM D-3279 method. The content of insolubles in heptane has to be reduced to less than 0.5% by weight, preferably to less than 0.1%.

According to a specific embodiment, the stage of pretreatment a0) by filtration comprises at least one filter, the size of the pores of which is less than 10 μm and preferably greater than 5 μm, followed by a filtration system, the size of the pores of which is less than 2 μm and preferably less than 1 μm.

According to another specific embodiment, the stage of pretreatment a0) by filtration comprises at least one filter, the size of the pores of which is less than 10 μm and preferably greater than 5 μm, followed by an electrostatic precipitation system.

According to another specific embodiment, the stage of pretreatment a0) by filtration comprises at least one filter, the size of the pores of which is less than 10 μm and preferably greater than 5 μm, followed by a system of filter(s) using filtration adjuvants, such as sand or diatomaceous earths.

According to another alternative form, said optional pretreatment stage a0) is carried out by centrifugation. According to another alternative form, the pretreatment stage a0) comprises a centrifugation and a filtration.

According to another alternative form, said optional pretreatment stage a0) comprises a selective hydrogenation stage. This selective hydrogenation stage is advantageously carried out in a reaction section fed at least with said feedstock, optionally pretreated by one or more pretreatments described above, and a gas stream comprising hydrogen, in the presence of at least one selective hydrogenation catalyst, at a 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 hydrogenated effluent.

This selective hydrogenation stage is carried out under hydrogen pressure and temperature conditions making 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 the pyrolysis oil. It is advantageously carried out under milder conditions than the hydrogenation stage a). 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 downstream reaction section(s). The styrene compounds, in particular styrene, possibly present in the feedstock can also behave like the diolefins in terms of

formation of gums owing to the fact that the double bond of the vinyl group is conjugated with the aromatic nucleus. Said selective hydrogenation stage makes it possible to obtain a selectively hydrogenated effluent, that is to say an effluent having a reduced content of olefins, in particular of diolefins and possibly of styrene compounds.

Said reaction section employs a selective hydrogenation, preferably in a fixed bed, in the presence of at least one selective hydrogenation catalyst, advantageously at an average temperature (or WABT as defined below for the hydrogenation stage a)) between 100 and 280°C, preferably between 120 and 260°C, in a preferred way between 130 and 250°C, a hydrogen partial pressure between 1.0 and 10.0 MPa abs., preferably between 2.0 and 8.0 MPa abs., and at an hourly space velocity (HSV) between 0.3 and 10.0 h^{-1}, preferably between 0.5 and 5.0 h^{-1}.

The amount of the gas stream comprising hydrogen (H_2) feeding said reaction section of the selective hydrogenation stage is advantageously such that the hydrogen coverage is of between 1 and 200 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3), preferably between 1 and 50 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3), in a preferred way between 5 and 20 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3).

The hourly space velocity (HSV) and the hydrogen coverage are as defined below for the hydrogenation stage a).

The selective hydrogenation stage is preferably carried out in a fixed bed. It can also be carried out in an ebullated bed or in a moving bed.

Advantageously, the reaction section of said selective hydrogenation stage comprises between 1 and 5 reactors. According to a specific embodiment of the invention, the reaction section comprises between 2 and 5 reactors, which operate in permutable mode, known as PRS for Permutable Reactor System or also “lead and lag” as described in the hydrogenation stage a). According to a particularly preferred alternative form, the selective hydrogenation reaction section comprises two reactors operating in permutable mode.

Said selective hydrogenation catalyst is generally a catalyst as described in the hydrogenation stage a). It can be identical to or different from the catalyst of the hydrogenation stage a).

The content of impurities, in particular of diolefins, of the hydrogenated effluent obtained on conclusion of the selective hydrogenation stage is reduced with respect to that of the same impurities, in particular of the diolefins, included in the feedstock of the process. The

selective hydrogenation stage generally makes it possible to convert at least 20% and preferably at least 30% of the diolefins contained in the initial feedstock.

Advantageously, said optional pretreatment stage a0) comprises a filtration stage and/or a centrifugation stage and/or an electrostatic separation stage and/or a stage of scrubbing by means of an aqueous solution and/or an adsorption stage, followed by a selective hydrogenation stage.

Said optional pretreatment stage a0) can also be optionally fed with at least a part of the hydrocarbon effluent resulting from stage c) of the process and/or a part of the first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C resulting from stage f) and/or a part of the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C resulting from stage f), as a mixture with or separately from the feedstock comprising a plastics pyrolysis oil. The recycle of at least a part of the liquid effluent resulting from stage c) and/or of at least a part of one or more hydrocarbon effluents resulting from stage f) makes it possible in particular to increase the sedimentation and thus, after an optional filtration, to improve the pretreatment of the feedstock.

Said optional pretreatment stage a0) thus makes it possible to obtain a pretreated feedstock which subsequently feeds stage b) and/or the hydrogenation stage a) when it is present.

Hydrogenation stage a) (optional)

According to the invention, the process optionally comprises a hydrogenation stage a) 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, which is optionally pretreated, and a gas stream comprising hydrogen, said hydrogenation reaction section being employed 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.

Stage a) 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 stage, 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 plastics pyrolysis oil, the hydrodemetallization of at least a part of the metals, in particular 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 the hydrotreating stage b). In parallel with the hydrogenation, the hydrodemetallization, and in particular the retention of silicon during stage a), makes it possible to limit the catalytic deactivation of the reaction section of the hydrotreating stage b). Furthermore, the conditions of stage a) make it possible to convert at least a part of the chlorine.

The control of the temperature is important in this stage and must satisfy an antagonistic constraint. On the one hand, the inlet temperature and the temperature throughout the hydrogenation reaction section must be sufficiently high in order to make possible the hydrogenation of the diolefins and olefins at the beginning of the hydrogenation reaction section. On the other hand, the inlet temperature of the hydrogenation reaction section must be sufficiently low in order to avoid deactivation of the catalyst. As hydrogenation reactions, in particular for hydrogenation of a part of the olefins and diolefins, are highly exothermic, an increasing temperature profile is therefore observed in the hydrogenation reaction section. This higher temperature at the end of said section makes it possible to carry out the hydrodemetallization and hydrodechlorination reactions. Thus, the outlet temperature of the reaction section of stage a) is greater than the inlet temperature of the reaction section of stage a), generally by at least 3°C, preferably by at least 5°C.

The temperature in stage a), whether this is the average temperature (WABT), the inlet temperature of the reaction section or also the rise in the temperature in stage a) between inlet and outlet of the reaction section, can in particular be controlled by injection of a diluent in stage a), preferably of a recycle of a part of the liquid effluent resulting from stage c) and/or of at least a part of one or more hydrocarbon effluents resulting from stage f), in particular by the recycle ratio and/or by the temperature of the recycled effluent.

The difference in temperature between the inlet and the outlet of the reaction section of stage a) is compatible with injection of a gaseous (hydrogen) or liquid cooling stream, in particular a part of the liquid hydrocarbon effluent resulting from stage c).

The difference in temperature between the inlet and the outlet of the reaction section of stage a) is exclusively due to the exothermicity of the chemical reactions carried out in the reaction section and thus does not include use of a heating means (oven, heat exchanger, and the like).

The inlet temperature of the reaction section of stage a) is of between 135 and 397°C, preferably between 240 and 347°C.

The outlet temperature of the reaction section of stage a) is of between 138 and 400°C, preferably between 243 and 350°C.

According to the invention, it is advantageous to carry out the hydrogenation of the diolefins and a part of the hydrodemetallization reactions in one and the same stage and at a temperature sufficient to limit the deactivation of the catalyst of stage a), which manifests itself by a decrease in the conversion of the diolefins. This same stage also makes it possible to benefit from the heat from hydrogenation reactions, in particular reactions for hydrogenation of a part of the olefins and diolefins, so as to have an increasing temperature profile in this stage and thus to be able to eliminate the need for a heating device between the catalytic hydrogenation section and the catalytic hydrotreating section.

Said reaction section carries out a hydrogenation in the presence of at least one hydrogenation catalyst, advantageously at an average temperature (or WABT as defined below) between 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}.

According to the invention, the “average temperature” of a reaction section corresponds to the weight-average bed temperature (WABT), which is well known to a person skilled in the art. The average temperature is advantageously determined as a function of the catalytic systems, of the items of equipment, of the configuration of these, which 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 effluent at the inlet of the reaction section, 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 comprising the plastics pyrolysis oil, which has optionally been pretreated, to the volume of catalyst(s).

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 "fresh" feedstock, that is to say of the feedstock to be treated, which has optionally been pretreated, without taking into account a recycled fraction, and in particular without taking into account the recycled liquid effluent resulting from stage c) and/or the liquid effluent resulting from stage f), at 15°C (in standard m^3, denoted Sm^3, of H_2 per m^3 of feedstock).

The amount of the gas stream comprising hydrogen (H_2) feeding said reaction section of stage a) is advantageously such that the hydrogen coverage is of between 100 and 1500 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3), preferably between 200 and 1000 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3), in a preferred way between 250 and 800 Sm^3 of hydrogen per m^3 of feedstock (Sm^3/m^3).

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

Advantageously, the reaction section of said stage a) 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 alternative form, 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 alternative form, the hydrogenation reaction section of stage a) comprises two reactors operating in permutable mode.

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 an alternative form, 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 alternative form, the total content, expressed as oxides, of the metal elements from groups VIB and VIII is preferably of between 1% and 40% by weight, preferentially from 5% to 30% by weight, with respect to the total weight of the catalyst. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively. When the metal is molybdenum or tungsten, the metal content is expressed as MoO_3 and WO_3 respectively.

The ratio by weight, expressed as metal oxide, of the metal (or metals) from group VIB with respect to the metal (or to the metals) from group VIII is preferably of between 1 and 20 and in a preferred way between 2 and 10.

According to this alternative form, the reaction section of said stage a) 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 with respect 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 MoO_3 with respect to the weight of said catalyst), on a preferably inorganic support, preferably on an alumina support.

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

The support of said hydrogenation catalyst is preferably chosen from alumina, silica, silicas-aluminas, magnesia, clays and their mixtures. 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, with respect to the weight of the alumina, and advantageously at least 0.001% by weight, with respect to the total weight of the alumina. When boron trioxide B_2O_3 is present, its concentration is less than 10% by weight, with respect to the weight of the alumina, and advantageously at least 0.001%, with respect 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, stage a) can employ, in addition to the hydrogenation catalyst(s) described above, moreover at least one hydrogenation catalyst used in stage a) 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 with respect 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 with respect 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, stage a) can employ, upstream of the hydrogenation catalyst(s), at least one guard bed containing adsorbents of alumina, silica-alumina, zeolite and/or active 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 stage a) 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. The content of impurities, in particular of diolefins, of the hydrogenated effluent obtained on conclusion of stage a) is reduced with respect to that of the same impurities, in particular of the diolefins, included in the feedstock of the process. The hydrogenation stage a) 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 hydrotreating reactions, in particular the removal, at least partly, of other contaminants, such as, for example, silicon and chlorine. Preferably, at least 50% and more preferentially at least 75% of the chlorine and of the silicon of the initial feedstock are removed during stage a). The hydrogenated effluent obtained on conclusion of the hydrogenation stage a) is sent, preferably directly, to the hydrotreating stage b).

Hydrotreating stage b)

According to the invention, the treatment process comprises a hydrotreating stage b) carried out in a hydrotreating reaction section comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with the feedstock, optionally pretreated in stage a0), or said hydrogenated effluent resulting from stage a) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed 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, stage b) carries out hydrotreating reactions well known to a person skilled in the art and more particularly hydrotreating reactions such as the hydrogenation of aromatics, hydrodesulfurization and hydrodenitrogenation. Furthermore, the hydrogenation of the olefins and of the remaining halogen compounds and also the hydrodemetallization are continued.

Said hydrotreating reaction section is advantageously employed at a pressure equivalent to that used in the reaction section of the hydrogenation stage a), and generally at a higher average temperature than that of the reaction section of the hydrogenation stage a). Thus, said hydrotreating reaction section is advantageously implemented at an average hydrotreating 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}, preferably between 0.1 and 5.0 h^{-1}, preferentially between 0.2 and 2.0 h^{-1}, in a preferred way between 0.2 and 1 h^{-1}. The hydrogen coverage in stage b) is advantageously of between 100 and 1500 Sm^3 of hydrogen per m^3 of fresh feedstock, preferably between 200 and 1000 Sm^3 of hydrogen per m^3 of fresh feedstock and in a preferred way between 250 and 800 Sm^3 of hydrogen per m^3 of fresh feedstock. The definitions of the average temperature (WABT), of the HSV and of the hydrogen coverage correspond to those described above.

The hydrotreating stage is preferably carried out in a fixed bed. It can also be carried out in an ebullated bed, in an entrained bed or in a moving bed. When the hydrotreating stage is carried out in an ebullated bed, in an entrained bed or in a moving bed, an additional stage of hydrotreating in a fixed bed can be carried out, under the same ranges of operating conditions, after that in an ebullated bed, in an entrained bed or in a moving bed, with or without intermediate separation of a gas stream.

Preferably, the treatment process comprises a hydrotreating stage b) carried out in a hydrotreating 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 hydrotreating catalyst.

Said hydrotreating reaction section is fed at least with the feedstock or said hydrogenated effluent resulting from stage a) and a gas stream comprising hydrogen, advantageously at the first catalytic bed of the first reactor in operation. An injection of at least a part of the feedstock or of the hydrogenated effluent resulting from stage a) and/or at least a part of hydrogen between the different catalytic beds is also possible. Optionally, the reaction section of said stage b) can furthermore also be fed with at least a part of the liquid effluent resulting from stage c) and/or with at least a part of one of the effluents from stage f).

Advantageously, said stage b) is carried out in a hydrotreating 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 1, preferably of between 1 and 10, in a preferred way between 2 and 5, said bed(s) each comprising at least one and preferably not more than ten hydrotreating catalyst(s). When a reactor comprises several catalytic beds, that is to say at least two, preferably between two and ten, in a preferred way between two and five, catalytic beds, said catalytic beds are preferably arranged in series in said reactor.

When stage b) is carried out in a hydrotreating reaction section comprising several reactors, preferably two reactors, these reactors can operate in series and/or in parallel and/or in permutable (or PRS) mode and/or in swing mode. The various optional operating modes, PRS (or lead and lag) mode and swing mode, are well known to a person skilled in the art and are advantageously defined above.

In another embodiment of the invention, said hydrotreating reaction section comprises a single fixed-bed reactor containing n catalytic beds, n being an integer greater than or equal to 1, preferably of between 1 and 10, preferably of between 2 and 5.

In a particularly preferred embodiment, the hydrogenation reaction section of stage a) comprises two reactors operating in permutable mode, followed by the hydrotreating reaction section of stage b) which comprises a single fixed-bed reactor.

Advantageously, said hydrotreating catalyst used in said stage b) can be chosen from known hydrodemetallization, hydrotreating or silicon-scavenging catalysts, used in particular for the

treatment of petroleum cuts, and their combinations. 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 hydrotreating 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 hydrotreating catalyst comprises a support, preferably an inorganic 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, with respect to the total weight of the catalyst. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively. When the metal is molybdenum or tungsten, the metal content is expressed as MoO_3 and WO_3 respectively. The ratio by weight, expressed as metal oxide, of the metal (or metals) from group VIB, with respect to the metal (or metals) from group VIII, is preferably of between 1.0 and 20, in a preferred way between 2.0 and 10. For example, the hydrotreating reaction section of stage b) of the process comprises a hydrotreating 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, with respect to the total weight of the hydrotreating catalyst, and between 1.0% and 30% by weight of molybdenum, preferably between 3.0% and 29% by weight of molybdenum, expressed as molybdenum oxide MoO_3, with respect to the total weight of the hydrotreating catalyst, on an inorganic support, preferably on an alumina support.

The support of said hydrotreating catalyst is advantageously chosen from alumina, silica, silicas-aluminas, magnesia, clays and their mixtures. 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. Preferably, said hydrotreating catalyst comprises an alumina support, preferably an alumina support doped with phosphorus and optionally boron. When phosphorus pentoxide P_2O_5 is present, its concentration is less than 10% by weight, with respect to the weight of the alumina, and advantageously at least 0.001% by weight, with respect to the total weight of

the alumina. When boron trioxide B_2O_3 is present, its concentration is less than 10% by weight, with respect to the weight of the alumina, and advantageously at least 0.001%, with respect to the total weight of the alumina. The alumina used can, for example, be a γ (gamma) or η (eta) alumina.

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

Advantageously, said hydrotreating catalyst used in stage b) of the process exhibits a specific surface of greater than or equal to 250 m^2/g, preferably of greater than or equal to 300 m^2/g. The specific surface of said hydrotreating catalyst is advantageously of less than or equal to 800 m^2/g, preferably of less than or equal to 600 m^2/g, in particular of less than or equal to 400 m^2/g. The specific surface of the hydrotreating catalyst is measured by the BET method, that is to say the specific surface determined by nitrogen adsorption in accordance with Standard ASTM D 3663-78 established from the Brunauer-Emmett-Teller method described in the periodical *The Journal of the American Chemical Society*, 60, 309 (1938). Such a specific surface makes it possible to further improve the removal of the contaminants, in particular of the metals, such as silicon.

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

In a preferred way, stage b) can employ, upstream of the hydrogenation catalyst(s), at least one guard bed or a series of guard beds of “grading” type as described above for stage a).

Advantageously, the hydrotreating stage b) makes possible the hydrogenation of at least 80% and preferably of all of the olefins remaining after the hydrogenation stage a), but also the conversion, at least partly, of other impurities present in the feedstock, such as the aromatic compounds, the metal compounds, the sulfur compounds, the nitrogen compounds, the halogen compounds (in particular the chlorine compounds) and the oxygen compounds. Preferably, the nitrogen content at the outlet of stage b) is less than 100 ppm by weight. Preferably, the sulfur content at the outlet of stage b) is less than 100 ppm by weight. Stage b) can also make it possible to further reduce the content of contaminants, such as that of the metals, in particular the silicon content. Preferably, the content of metals at the outlet of

stage b) is less than 10 ppm by weight, in a preferred way less than 2 ppm by weight, and the silicon content is less than 5 ppm by weight.

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 stage a0), of the optional hydrogenation stage a) and/or of the hydrotreating stage b) and/or upstream of one of the optional hydrocracking stages g), when they are present, preferably upstream of the hydrogenation stage a) and/or the hydrotreating stage b), in order to ensure a sufficient amount of sulfur to form the active entity of the catalyst (in sulfide form).

This activation or sulfidation stage is carried out by methods well known to a person skilled in the art, and advantageously under a sulfo-reductive atmosphere in the presence of hydrogen and hydrogen sulfide. The sulfiding agents are preferably H_2S gas, elemental sulfur, CS_2, mercaptans, sulfides and/or polysulfides, hydrocarbon cuts having a boiling point of less than 400°C containing sulfur compounds or any other sulfur-containing compound used for the activation of hydrocarbon feedstocks with a view to sulfiding the catalyst. Said sulfur-containing compounds are advantageously chosen from alkyl disulfides, such as, for example, dimethyl disulfide (DMDS), alkyl sulfides, such as, for example, dimethyl sulfide, thiols, such as, for example, n-butyl mercaptan (or 1-butanethiol), and polysulfide compounds of tert-nonyl polysulfide type. The catalyst can also be sulfided by the sulfur contained in the feedstock to be desulfurized. Preferably, the catalyst is sulfided *in situ* in the presence of a sulfiding agent and of a hydrocarbon feedstock. Very preferably, the catalyst is sulfided *in situ* in the presence of the feedstock additivated with dimethyl disulfide.

The injection of a sulfiding agent is in particular necessary at the start of the catalytic cycle, the time that the H_2S is formed in order to be separated in stage d) and recycled upstream of stage a) and/or of stage b) and/or of stage g), or also upstream of the selective hydrogenation stage of the pretreatment a0). Additional injections throughout the catalytic cycle may be necessary in order to compensate for the natural loss. However, the fact of being able to recycle a gas phase containing the H_2S without the NH_3 by the present invention makes it possible to considerably reduce the consumption of the sulfiding agent.

Separation stage c)

According to the invention, the treatment process comprises a separation stage c), advantageously carried out in at least one scrubbing/separation section, fed at least with the hydrotreated effluent resulting from stage b), and optionally with the hydrocracked effluent

resulting from the optional stages g) and g'), and an aqueous solution, in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent.

The gaseous effluent obtained on conclusion of stage c) advantageously comprises hydrogen, preferably comprises at least 80% by volume, preferably at least 85% by volume, of hydrogen. Advantageously, said gaseous effluent can, at least partly, be recycled to the hydrogenation stage a) and/or the hydrotreating stage b) and/or the hydrocracking stage g), it being possible for the recycling system to comprise a purification section.

The gaseous effluent can also form the subject of additional separation(s) for the purpose of recovering at least one hydrogen-rich gas and/or light hydrocarbons, in particular ethane, propane and butane, which can advantageously be sent separately or as a mixture to one or more furnaces of the steam cracking stage h) so as to increase the overall yield of olefins.

The hydrocarbon effluent resulting from the separation stage c) is sent, partly or completely, either directly to the inlet of a steam cracking unit or to an optional fractionation stage f). Preferably, the liquid hydrocarbon effluent is sent, partly or completely, to a fractionation stage f).

The first aqueous effluent obtained on conclusion of stage c) advantageously comprises ammonium salts and/or hydrochloric acid, and also dissolved H_2S and NH_3.

This separation stage c) makes it possible in particular to remove the ammonium chloride salts, which are formed by reaction between the chloride ions, released by the hydrogenation of the chlorine compounds in HCl form, in particular during stages a) and b), followed by dissolution in the water, and the ammonium ions, generated by the hydrogenation of the nitrogen compounds in NH_3 form, in particular during stage b), and/or contributed by the injection of an amine, followed by dissolution in the 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. It also makes it possible to remove the hydrochloric acid formed by the reaction of the hydrogen ions and the chloride ions. This stage c) also makes it possible to remove the ammonium sulfide salts ($(NH_4)_2S$) which are formed by reaction between the H_2S resulting from the hydrodesulfurization of the sulfur compounds and the NH_3.

As a function of the content of chlorine compounds in the initial feedstock to be treated, a stream containing a nitrogen compound, such as an amine, for example monoethanolamine,

diethanolamine and/or monodiethanolamine, can be injected upstream of the selective hydrogenation stage of the pretreatment a0) and/or upstream of the hydrogenation stage a) and/or between the hydrogenation stage a) and the hydrotreating stage b) and/or between the hydrocracking stage g) and the separation stage c), preferably upstream of the hydrogenation stage a), in order to ensure a sufficient amount of ammonium ions to combine with the chloride ions formed during the hydrotreating stage, thus making it possible to limit the formation of hydrochloric acid and thus to limit the corrosion downstream of the separation section.

According to an alternative form, said gas phase containing the NH_3 resulting from stage e) can also be used as nitrogen compound.

Advantageously, the separation stage c) comprises an injection of an aqueous solution, preferably an injection of water, into the hydrotreated effluent resulting from stage b), or the hydrocracked effluent resulting from the optional stage g), upstream of the scrubbing/separation section, so as to dissolve, at least partly, ammonium chloride salts and/or hydrochloric acid and thus to improve the removal of the chlorinated impurities and to reduce the risks of pluggings due to an accumulation of the ammonium chloride salts.

The separation stage c) is advantageously carried out at a temperature of between 20 and 450°C, preferentially between 100 and 440°C, preferably between 200 and 420°C. It is important to operate in this temperature range (and thus not to excessively cool the hydrotreated effluent) at the risk of plugging in the lines due to the precipitation of the ammonium chloride salts. Advantageously, the separation stage c) is carried out at a pressure close to that employed in stages a) and/or b), preferably between 1.0 and 10.0 MPa, so as to facilitate the recycling of hydrogen.

The separation stage can advantageously be carried out by any method known to a person skilled in the art, such as, for example, the combination of one or more separator(s) (drum(s)) 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. The scrubbing/separation section of stage c) can, at least partly, be made of common or separate items of scrubbing and separation equipment.

In an optional embodiment of the invention, the separation stage c) comprises the injection of an aqueous solution into the hydrotreated effluent resulting from stage b), followed by the scrubbing/separation section advantageously comprising a phase of separation which makes it possible to obtain at least one first aqueous effluent charged with ammonium salts, a

scrubbed liquid hydrocarbon effluent and a partially scrubbed gaseous effluent. Said first aqueous effluent charged with ammonium salts and the scrubbed liquid hydrocarbon effluent can subsequently be separated in a knockout drum in order to obtain said hydrocarbon effluent and said first aqueous effluent. Said partially scrubbed gaseous effluent can, in parallel, be introduced into a scrubbing column where it circulates countercurrentwise to an aqueous stream, preferably of the same nature as the aqueous solution injected into the hydrotreated effluent, which makes it possible to remove, at least partly, preferably completely, the hydrochloric acid contained in the partially scrubbed gaseous effluent and to thus obtain said gaseous effluent, preferably essentially comprising hydrogen, and an acidic aqueous stream. Said first aqueous effluent resulting from the knockout drum can 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 for feeding the separation stage c) with said aqueous solution upstream of the scrubbing/separation section and/or with said aqueous stream in the scrubbing 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 dissolved salts.

In another optional embodiment of the invention, the separation stage c) can advantageously comprise a “high-pressure” scrubbing/separation section which operates at a pressure close to the pressure of the hydrogenation stage a) and/or of the hydrotreating stage b) and/or of the optional hydrocracking stage g), preferably between 1.0 and 10.0 MPa, in order to facilitate the recycling of hydrogen. This optional “high-pressure” section of stage c) can be supplemented by a “low-pressure” section, in order to obtain a hydrocarbon effluent devoid of a portion of the gases dissolved at high pressure and intended to be treated directly in a steam cracking process or optionally to be sent into the fractionation stage f).

Variant two-stage separation stage c)

In an optional embodiment of the invention, the separation stage c) comprises the following substages:

c1) a separation stage, fed with the hydrotreated effluent resulting from stage b), said stage being carried out at a temperature of between 200 and 450°C and at a pressure substantially identical to the pressure of stage b), in order to obtain at least a gaseous effluent and a liquid effluent, a part of which can be recycled upstream of stage a) and/or of stage b),

c2) a separation stage, fed with the gaseous effluent resulting from stage c1) and another part of the liquid effluent resulting from stage c1) and an aqueous solution, said stage being carried out at a temperature of between 20 and less than 200°C and at a pressure

substantially identical to or less than the pressure of stage b), in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent.

Stage c1)

According to the invention, the treatment process can comprise a separation stage c1), fed with the hydrotreated effluent resulting from stage b), said stage being carried out at a temperature of between 200 and 450°C and at a pressure substantially identical to the pressure of stage b), in order to obtain at least a gaseous effluent and a liquid effluent, a part of which can be recycled upstream of stage a) and/or of stage b).

The separation stage c1) is a separation stage said to be a high-pressure or medium-pressure high-temperature separation stage, also known to a person skilled in the art under the name HHPS (Hot High Pressure Separator). Thus, this stage c1) preferably employs a "hot high-pressure" separator, the pressure being substantially equal to the operating pressure of stage b). The term "pressure substantially equal to the pressure of stage b)" is understood to mean the pressure of stage 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 0.2 MPa, with respect to the pressure of stage b). Preferably, the pressure of stage c1) is the pressure of stage b) decreased by pressure drops.

The temperature at which the separation is carried out is of between 200 and 450°C, preferably of between 220 and 330°C and particularly preferably of between 240 and 300°C. According to a preferred alternative form, and with a view to recovering the most heat, the separation is carried out at a temperature which is the highest possible but less than or equal to the outlet temperature of stage b), which makes it possible to avoid or to limit reheating (and thus a need for heat) of the effluent from stage b). According to another alternative form, the effluent from stage b) can be reheated or cooled before the separation.

This separation stage c1) can advantageously be carried out by any method known to a person skilled in the art, such as, for example, the combination of one or more separator(s) (drum(s)) 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, stage c) is carried out with a single separator (drum).

A part of the liquid effluent can be recycled upstream of stage a) and/or of stage b) and/or upstream of the selective hydrogenation stage of the pretreatment a0). The recycling of a

part of the product obtained to or upstream of at least one of the reaction stages advantageously makes it possible, on the one hand, to dilute the impurities and, on the other hand, to control the temperature in the reaction stage(s), in which the reactions involved can be highly exothermic.

Advantageously, the amount of recycled liquid effluent resulting from stage c), that is to say the recycled fraction of product obtained, is adjusted so that the ratio by weight of the recycle stream from stage c) to the feedstock comprising a plastics pyrolysis oil, that is to say 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, preferably greater than or equal to 0.01 and in a preferred way greater than or equal to 0.1. Preferably, the amount of recycled liquid effluent resulting from stage c) is adjusted so that the ratio by weight of the recycle stream to the feedstock comprising a plastics pyrolysis oil is of between 0.01 and 10, preferably of between 0.1 and 7 and particularly preferably of between 0.2 and 5. This recycle ratio makes it possible in particular to control the rise in the temperature in stage a). 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 stage a), in particular due to the hydrogenation reactions of the diolefins, is thus controllable by the dilution effect.

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 stage a) and/or stage b) can be at least partly contributed by the heat of a part of the liquid effluent resulting from stage c) 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 fact of recycling at least a part of the liquid effluent at high pressure makes it possible to economize on energy for its pressurization in stage a) and/or stage b).

The high-pressure and high-temperature separation makes it possible, on the other hand, to minimize the amount of light fraction (hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C or naphtha) contained in the liquid effluent recycled in stage a) and/or stage b). At this temperature, virtually all of the light fraction of the effluent (naphtha) leaves as gaseous effluent to the separation/scrubbing stage c2), whereas, as liquid phase, there is predominantly the heavy fraction of the feedstock

(hydrocarbon cut comprising compounds having a boiling point of greater than 175°C or middle distillates). In this way, the pH_2p is favoured in stage a) and/or in stage b) because the light fraction (naphtha) might partly evaporate and lower the pH_2p 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 stage c1), even if this use is not preferred as a result of the energy loss linked to the pressure reduction. Another option for increasing the removal of the light faction comprising naphtha can consist in carrying out a stripping, for example by injecting a hydrogen-rich gas in stage c1).

According to a preferred alternative form, at least a part of the hydrotreated liquid effluent resulting from stage c) can advantageously be either cooled, or preheated, if necessary, or kept at the same temperature as at the outlet of the separation stage c), before being advantageously recycled upstream of the hydrogenation stage a) and/or of the hydrotreating stage b), according to the temperature and the flow rate of feedstock and hydrogen, so that the temperature of the incoming stream, comprising said feedstock as a mixture with at least a part of said liquid effluent resulting from stage c) and a hydrogen-rich gas, is of between 140 and 430°C, preferably between 220 and 350°C and particularly preferably between 260 and 330°C.

In the case where at least a part of the liquid effluent resulting from the separation stage c) is preheated before being recycled upstream of stage a) and/or stage b), said effluent optionally passes through at least one exchanger and/or at least one oven before being recycled upstream of stage a) and/or stage b), so as to adjust the temperature of said recycled liquid effluent.

In the case where at least a part of the liquid effluent resulting from the separation stage c) is cooled before being recycled upstream of stage a) and/or stage b), said effluent optionally passes through at least one exchanger and/or at least one cooling tower before being recycled upstream of stage a) and/or stage b), so as to adjust the temperature of said recycled liquid effluent.

The use of the recycle, upstream of the hydrogenation stage a) and/or upstream of the hydrotreating stage b), of at least a part of the liquid effluent resulting from stage c), which can be either cooled or preheated, if necessary, or kept at the same temperature as at the outlet of the separation stage c), thus makes it possible to adjust the temperature of the stream entering stage a) and/or stage b), as needed.

According to an alternative form, the feedstock, before being mixed with at least a part of the effluent resulting from stage c), 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. 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 at least a part of the effluent resulting from stage c). 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. According to another alternative form, the heating of the feedstock to a temperature above 150°C, preferably above 180°C and particularly preferably above 200°C is carried out by ovens or exchangers proportioned in order to have a very low wall temperature in comparison with the temperature of the feedstock, for example an electric oven.

According to another alternative form, the feedstock is entirely heated by indirect heating by at least a part of the effluent resulting from stage c). In this case, the feedstock is not preheated before being mixed with at least a part of the effluent resulting from stage c).

According to another alternative form, the feedstock is not heated by indirect heating by at least a part of the effluent resulting from stage c). In this case, the feedstock and the part of the recycled effluent resulting from stage c) are mixed, the part of the recycled effluent resulting from stage c) having substantially the same temperature as or a lower temperature than the feedstock.

Another heating stream advantageously consists of a hydrogen-rich gaseous effluent originating from the hydrogen supply and/or of the gaseous effluent resulting from the separation stage c). At least a part of this hydrogen-rich gaseous effluent originating from the hydrogen supply and/or of the gaseous effluent resulting from the separation stage c) is advantageously injected as a mixture with at least a part of the liquid effluent resulting from stage c) or separately, upstream of stage a) and/or of stage b). The hydrogen-rich gas stream can thus be advantageously either preheated as a mixture with at least a part of the liquid effluent or preheated separately before mixing, preferably by optional passage through at least one exchanger and/or at least one oven or any other heating means known to a person skilled in the art.

Stage c2)

According to the invention, the treatment process comprises a separation stage c2), advantageously carried out in at least one scrubbing/separation section, fed with the first gaseous effluent and another part of the liquid effluent resulting from stage c1) and an aqueous solution, said stage being carried out at a temperature of between 20 and less than 200°C and at a pressure substantially identical to or less than the pressure of stage b), in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent.

The separation stage c2) is carried out in at least one knockout drum said to be a high-pressure or medium-pressure low-temperature knockout drum, also known to a person skilled in the art under the name CHPS (Cold High Pressure Separator). Thus, this stage c2) preferably employs a “cold high-pressure” separator, the pressure being substantially equal to the operating pressure of stage b). The term “pressure substantially equal to the pressure of stage b)” is understood to mean the pressure of stage 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 0.2 MPa, with respect to the pressure of stage b). Preferably, the pressure of stage c2) is the pressure of stage b) decreased by pressure drops. The fact of operating at least a part of the separation stage c2) at a pressure substantially identical to the operating pressure of stage b) furthermore facilitates the recycling of hydrogen.

The separation stage c2) can also be carried out at a lower pressure than the pressure of stage b).

The separation stage c2) can also comprise a (first) stage of separation at a pressure substantially equal to the operating pressure of stage b), followed by at least one other separation stage carried out at a temperature identical to or lower than and at a pressure lower than each preceding separation stage of stage c2).

The temperature at which the separation of stage c2) is carried out is of between 20 and less than 200°C, preferably of between 25 and 120°C and particularly preferably of between 30 and 70°C.

It is important to operate in this temperature range (and thus to not excessively cool the hydrotreated effluent) at the risk of plugging in the lines due to the precipitation of the ammonium chloride salts.

The scrubbing/separation section of stage c2) can at least partly be made of common or separate items of scrubbing and separation equipment, these items of equipment being well known (knockout drums which can be operated at various pressures and temperatures, pumps, heat exchangers, scrubbing columns, and the like). The separation stage c2) can in particular be carried out the same as stage c) described above.

When one (or two) hydrocracking stages are present (described below), this stage c2) can in addition be fed with at least a part of the hydrocracked effluent resulting from an optional hydrocracking stage g).

At least a part of the hydrocarbon effluent resulting from stage c2) can be recycled as liquid quench upstream of stage a) and/or of stage b) and/or of stage g). The injection of the hydrocarbon effluent resulting from stage c2) can be carried out at the first catalytic bed of the reaction section of stage a) and/or of stage b) and/or of stage g) or between the different catalytic beds of each section. When the hydrogenation reaction section of stage a) comprises two reactors operating in permutable mode, at least a part of the hydrocarbon effluent resulting from stage c2) can be recycled between the two reactors.

Stage d) of separation of the H_2S contained in the first aqueous effluent

According to the invention, the treatment process comprises a stage d) of separation of the H_2S contained in the first aqueous effluent, in order to obtain a gas phase containing the H_2S and a second aqueous effluent, said gas phase containing the H_2S being preferably, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g).

Stage d) of separation of the H_2S contained in the first aqueous effluent is advantageously carried out by stripping using a gas stream, preferably an inert gas stream, in a stripping column. A stripping column is a distillation column in which a gas stream, preferably an inert gas stream, is injected at the column bottom. The gas phase containing the H_2S is recovered at the column top and a second aqueous effluent is recovered at the bottom of the column. The inert gas stream can be hydrogen, nitrogen or steam. Preferably, stage d) is carried out by steam stripping.

Stripping using a gas stream, preferably an inert gas stream, makes it possible to obtain a very low content of dissolved H_2S in the second aqueous effluent at the bottom of the stripping column.

The stage d) of separation of the H_2S is generally carried out at a pressure of between 0.5 and 1.5 MPa, preferably of between 0.5 and 1 MPa and particularly preferably of between 0.6 and 0.9 MPa.

The stripping is generally carried out at a temperature of between 80 and 150°C, preferably between 120 and 145°C (at the top and bottom of the column, respectively).

The flow rate of the inert gas stream is generally such that the ratio of the flow rate of the inert gas stream, expressed in standard m^3 per hour (Sm^3/h), to the flow rate of first aqueous effluent to be treated, expressed in m^3 per hour at standard conditions (15°C, 0.1 MPa), is of between 50 and 600 Sm^3/m^3, preferably between 200 and 400 Sm^3/m^3. Standard m^3 is understood to mean the amount of gas in a volume of 1 m^3 at 0°C and 0.1 MPa.

The stripping carried out under these operating conditions makes it possible in particular to separate H_2S from said first aqueous effluent without entraining the NH_3 (which remains predominantly in the aqueous phase).

According to an alternative form, in stage d), a part of the gas phase at the top of the stripping column, comprising the H_2S and the inert gas stream (steam), is condensed and is preferably reinjected, at least partly, as liquid reflux into the upper part of the stripping column. The condensation is generally carried out by cooling to a temperature of between 30 and 65°C, for example with cold water.
The liquid reflux makes it possible to control/reduce the temperature at the stripping column top.

Said gas phase containing the H_2S withdrawn at the stripping column top is at least partly recycled upstream of stage a) and/or stage b) and/or also upstream of the hydrocracking stage g) and/or upstream of the selective hydrogenation stage of the pretreatment a0), when they are present, in order to act as sulfiding agent for the catalyst(s). Before its recycling, it can be subjected to at least one additional stage of purification, for example a contacting with liquid or a scrubbing with amines.

According to another alternative form, stage d) of separation of the H_2S contained in the first aqueous effluent can also be carried out by liquid/liquid extraction, in which an inert solvent or a reactant is brought into contact with the aqueous effluent.

Stage e) of separation of the NH_3 contained in the second aqueous effluent

According to the invention, the treatment process comprises a stage e) of separation of the NH_3 contained in the second aqueous effluent resulting from stage d), in order to obtain a gas phase containing the NH_3 and a third aqueous effluent, said gas phase containing the NH_3 being preferably, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g).

Stage e) of separation of the NH_3 contained in the second aqueous effluent is advantageously carried out by stripping using an inert gas stream in a stripping column. The gas phase containing NH_3 is recovered at the column top and a third aqueous effluent is recovered at the bottom of the column. The inert gas stream can be hydrogen, nitrogen or steam. Preferably, stage e) is carried out by steam stripping.
The stripping using an inert gas stream makes it possible to obtain a very low content of dissolved NH_3 at the bottom of the stripping column, making it possible to recover a third aqueous effluent which can be introduced into a conventional wastewater treatment.

Stage e) of separation of the NH_3 is generally carried out at a pressure of between 0.1 and less than 0.5 MPa, preferably of between 0.05 and 0.2 MPa.

The stripping is generally carried out at a temperature of between 80 and 150°C, preferably between 120 and 145°C (at the top and bottom of the column, respectively).

The flow rate of the inert gas stream is generally such that the ratio of the flow rate of the inert gas stream, expressed in standard m^3 per hour (Sm^3/h), to the flow rate of feedstock to be treated, expressed in m^3 per hour at standard conditions (15°C, 0.1 MPa), is of between 50 and 600 Sm^3/m^3, preferably between 200 and 400 Sm^3/m^3. Standard m^3 is understood to mean the amount of gas in a volume of 1 m^3 at 0°C and 0.1 MPa.

According to an alternative form, in stage e), a part of the gas phase at the top of the stripping column, comprising the NH_3 and the inert gas stream (steam), is condensed and is preferably reinjected, at least partly, as liquid reflux into the upper part of the stripping column. The condensation is generally carried out by cooling to a temperature of between 30 and 65°C, for example with cold water.
The liquid reflux makes it possible to control/reduce the temperature at the stripping column top.

According to an alternative form, said gas phase containing the NH_3 can be, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g), and/or also upstream of the selective hydrogenation stage a0), advantageously in stoichiometric amounts suitable for the formation of the salts during the separation/scrubbing stage c).

Fractionation stage f) (optional)

The process according to the invention can comprise a stage of fractionation of all or part, preferably of the whole, of the hydrocarbon effluent resulting from stage c), in order to obtain at least a gas stream and at least two liquid hydrocarbon streams, said two liquid hydrocarbon streams being at least a first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C (naphtha cut), in particular between 80 and 175°C, and a second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C (middle distillates cut).

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

The optional fractionation stage f) is advantageously carried out at a pressure of less than or equal to 3.0 MPa abs., preferably between 0.5 and 2.5 MPa abs.

According to one embodiment, stage f) can be carried out in a section advantageously comprising at least one stripping column equipped with a reflux circuit comprising a reflux drum. Said stripping column is fed with the liquid hydrocarbon effluent resulting from stage c) and with a steam stream. The liquid hydrocarbon effluent resulting from stage c) can optionally be heated before entering the stripping column. Thus, the lightest compounds are entrained at the column top and into the reflux circuit comprising a reflux drum in which a gas/liquid separation takes place. The gas phase which comprises the light hydrocarbons is withdrawn from the reflux drum as a gas stream. The hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C is advantageously withdrawn from the reflux drum. The hydrocarbon cut comprising compounds having a boiling point of greater than 175°C is advantageously withdrawn at the stripping column bottom.

According to other embodiments, the fractionation stage f) can employ a stripping column followed by a distillation column or solely a distillation column.

According to the destination or the use of the cuts resulting from the fractionation stage f), 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.

The first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C and the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C, which are optionally mixed, can be sent, completely or partly, to a steam cracking unit, on conclusion of which olefins can be (re)formed 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 in at least one of the stages 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 feedstocks.

According to a preferred embodiment, the first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C is sent, completely or partly, to a steam cracking unit, whereas the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C is sent to a hydrocracking stage g) and/or sent to a fuel storage unit.

In a specific embodiment, the optional fractionation stage f) can make it possible to obtain, besides a gas stream, a naphtha cut comprising compounds having a boiling point of less than or equal to 175°C, preferably between 80 and 175°C, a middle distillates cut comprising compounds having a boiling point of greater than 175°C and less than 385°C and a hydrocarbon cut comprising compounds having a boiling point of greater than or equal to 385°C, known as heavy hydrocarbon cut. The naphtha cut can be sent, completely or partly, 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, completely or partly, either sent to a steam cracking unit, or to a unit for storage of diesel resulting from conventional petroleum feedstocks, or also be recycled; the heavy cut can, for its part, be sent, at least partly, to a steam cracking unit or be sent to the hydrocracking stage g), when it is present.

In another specific embodiment, the optional fractionation stage f) can make it possible to obtain, besides a gas stream, a naphtha cut comprising compounds having a boiling point of less than or equal to 175°C, preferably between 80 and 175°C, a kerosene cut comprising compounds having a boiling point of greater than 175°C and less than or equal to 280°C, a diesel cut comprising compounds having a boiling point of greater than 280°C and less than 385°C and a hydrocarbon cut comprising compounds having a boiling point of greater than or equal to 385°C, referred to as heavy hydrocarbon cut. The naphtha cut, the kerosene cut

and/or the diesel cut can be, completely or partly, 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 heavy cut can, for its part, be sent, at least partly, to a steam cracking unit or be sent to the hydrocracking stage g), when it is present.

In another specific embodiment, the naphtha cut comprising compounds having a boiling point of less than or equal to 175°C resulting from stage f) is fractionated to give a heavy naphtha cut comprising compounds having a boiling point between 80 and 175°C and a light naphtha cut comprising compounds having a boiling point of less than 80°C, at least a part of said heavy naphtha cut being sent to an aromatic complex comprising at least one stage 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 into the steam cracking stage h) described below.

The gaseous effluent(s) resulting from the fractionation stage f) can form the subject of 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 the steam cracking stage h) so as to increase the overall yield of olefins.

Hydrocracking stage g) (optional)

According to an alternative form, the process of the invention can comprise a hydrocracking stage g) carried out after the separation stage c) with at least a part of said hydrocarbon effluent resulting from stage c) or carried out after the fractionation stage f) with at least a part of the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C.

Advantageously, stage g) employs hydrocracking reactions well known to a person 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, contained in the hydrocarbon effluent resulting from the fractionation stage f). Other reactions, such as the hydrogenation of olefins or of aromatics, hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, and the like, can be pursued.

The compounds having a boiling point of greater than 175°C have a high BMCI and contain, with respect 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 stage g) 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 resulting from stage c) and/or with at least a part of the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C resulting from stage f) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed 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 employed at an average temperature between 250 and 450°C, preferably between 320 and 430°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 stage g) is advantageously of between 80 and 2000 Sm^3 of hydrogen per m^3 of fresh feedstock which feeds stage a) and preferably between 200 and 1800 Sm^3 of hydrogen per m^3 of fresh feedstock which feeds stage a). 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 stage a) or of the hydrotreating stage b).

Advantageously, said stage g) 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 1, preferably of between 1 and 10, in a preferred way of between 2 and 5, said bed(s) each comprising at least one, and preferably not more than ten, hydrocracking catalyst(s). When a reactor comprises several catalytic beds, that is

to say at least two, preferably between two and ten, in a preferred way between two and five, catalytic beds, said catalytic beds are preferably arranged in series in said reactor.

The hydrocracked effluent can, at least partly, be recycled in the hydrogenation stage a) and/or in the hydrotreating stage b) and/or in the separation stage c). Preferably, it is recycled in the separation stage c).

The hydrocracking stage can be carried out in one stage (stage g)) or two stages (stages g) and g')). When it is carried out in two stages, a separation of the effluent resulting from the first hydrocracking stage g) 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 stage g') comprising a dedicated second hydrocracking reaction section different from the first hydrocracking reaction section g). This configuration is particularly suitable when it is desired to produce only a naphtha cut.

The second hydrocracking stage g') 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 resulting from the first hydrocracking stage g) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed 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 stage are those described for the first hydrocracking stage. The operating conditions and catalysts used in the two hydrocracking stages can be identical or different.

Said second hydrocracking stage 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 1, preferably of between 1 and 10, in a preferred way of between 2 and 5, said bed(s) each comprising at least one, and preferably not more than ten, hydrocracking catalyst(s).

These operating conditions used in the hydrocracking stage(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, preferably of less than 160°C and in a preferred way of less than 150°C, 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 stages, the conversion per pass in the second stage is kept moderate in order to maximize the selectivity for compounds of the naphtha cut (having 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 stage. This ratio is defined as the ratio of the feed flow rate of stage g') to the flow rate of the feedstock of stage a) or of stage b); preferentially, this ratio is of between 0.2 and 4, in a preferred way between 0.5 and 2.5.

The hydrocracked effluent from the second hydrocracking stage g') can, at least partly, be recycled in the hydrogenation stage a) and/or in the hydrotreating stage b) and/or in the separation stage c). Preferably, it is recycled in the separation stage c).

The hydrocracking stage(s) thus does (do) not necessarily make it possible to convert all the hydrocarbon compounds having a boiling point of greater than 175°C (middle distillates cut) into hydrocarbon compounds having a boiling point of less than or equal to 175°C (naphtha cut). After the fractionation stage f), there may thus remain a more or less significant proportion of compounds having a boiling point of greater than 175°C. In order to increase the conversion, at least a part of this unconverted cut can be introduced into a second hydrocracking stage g'). 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, with respect to the incoming feedstock, and preferably between 0.5% and 5% by weight.

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

The hydrocracking catalyst(s) used in the hydrocracking stage(s) are conventional hydrocracking catalysts known to a person 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 specific surface area (generally 150 to 800 m^2/g) exhibiting a surface acidity, such as halogenated (in particular chlorinated or fluorinated) aluminas, combinations of boron and aluminium oxides, amorphous silicas-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, with respect to the total weight of the catalyst. When the metal is cobalt or nickel, the metal content is expressed as CoO and NiO respectively.

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, with respect to the total weight of the catalyst. When the metal is molybdenum or tungsten, the metal content is expressed as MoO_3 and WO_3 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 and 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 inorganic matrix of oxide type chosen from aluminas, silicas, silicas-aluminas, aluminates, alumina-boron oxide, magnesia, silica-magnesia, zirconia, titanium oxide or clay, alone or as a mixture, and preferably aluminas or silicas-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 with respect 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 an alternative form, the hydrocracking catalyst employed in the second hydrocracking stage 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), with respect to the total weight of the catalyst.

According to another aspect of the invention, the hydrocracking catalyst 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.

The preparation of the catalysts of the hydrogenation, hydrotreating and hydrocracking stages is known and generally comprises a stage 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 stage of the process, the catalysts are generally subjected to a sulfidation in order to form the active entity. The catalyst of stage a) can also be a catalyst used in its reduced form, thus involving a reduction stage in its preparation.

The gas stream comprising hydrogen, which feeds the selective hydrogenation, hydrogenation, hydrotreating and hydrocracking reaction section, can consist of a supply of hydrogen and/or can consist of recycled hydrogen resulting in particular from the separation stage c). 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.

Said hydrocarbon effluent or said hydrocarbon stream(s) thus obtained by treatment according to the process of the invention of a plastics pyrolysis oil exhibit(s) a composition compatible with the specifications for a feedstock at the inlet of a steam cracking unit. In particular, the composition of the hydrocarbon effluent or of said hydrocarbon stream(s) is preferably such that:

- the total content of metal elements is less than or equal to 10.0 ppm by weight, preferably less than or equal to 2.0 ppm by weight, preferentially less than or equal to 1.0 ppm by weight and in a preferred way less than or equal to 0.5 ppm by weight, with:

a content of silicon (Si) element of less than or equal to 5.0 ppm by weight, preferably of less than or equal to 1 ppm by weight and in a preferred way of less than or equal to 0.6 ppm by weight and/or 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 100 ppm by weight, preferably less than or equal to 50 ppm by weight, and/or

- the nitrogen content is less than or equal to 100 ppm by weight, preferably less than or equal to 50 ppm by weight and in a preferred way less than or equal to 5 ppm by weight, and/or

- the content of asphaltenes is less than or equal to 5.0 ppm by weight, and/or

- the total content of chlorine element is less than or equal to 10 ppm by weight, preferably less than 1.0 ppm by weight, and/or

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

- the content of olefinic compounds (mono-olefins and diolefins) is less than or equal to 5.0% by weight, preferably less than or equal to 2.0% by weight and in a preferred way less than or equal to 0.1% 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, with respect to the total weight of the stream under consideration.
The process according to the invention thus makes it possible to treat plastics pyrolysis oils in order to obtain an effluent which can be injected, completely or partly, into a steam cracking unit.

Stage (optional) of adsorption of heavy metals

Any gaseous effluent and/or any liquid effluent resulting from at least one of the separation stages c), d) or e) or from the fractionation stage f) can be subjected to an optional stage of adsorption of heavy metals.

The gaseous effluents can in particular be the gaseous effluent resulting from stage c) and/or the gas phase containing the H_2S resulting from stage d) and/or the gas phase containing NH_3 resulting from stage e) and/or the gaseous effluent resulting from the fractionation stage f).

The liquid effluents can in particular be the hydrocarbon effluent resulting from stage c) and/or the first and/or the second hydrocarbon cut resulting from stage f).

The optional adsorption stage 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 stages of the process according to the invention. Their transformed form is easier to trap. Their elimination or

reduction may in particular be necessary when a 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 stages, such as the fractionation stage f), to a stage having strict specifications for metal impurities, such as a steam cracking stage.

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

Said optional adsorption stage 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 stage 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 an alternative form, said optional adsorption stage is carried out in an adsorption section operated in the presence of at least one adsorbent comprising a porous support and 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, silicas-aluminas, silicas, zeolites and/or active carbons. Advantageously, the porous support is based on alumina. The specific surface of the support is generally of between 150 and 600 m^2/g, preferably between 200 and 400 m^2/g, more preferably still between 150 and 320 m^2/g. The specific surface of the adsorbent is a surface measured by the BET method, as described above.

The active phase is 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. Preferably, the active phase is in the metal sulfide form, in particular a sulfide of a metal from the group chosen from copper, molybdenum, tungsten, iron, nickel or cobalt.

Advantageously, the active phase of the adsorbent comprises between 1% and 70% by weight of sulfur, with respect to the total weight of the adsorbent, preferably between 2% and 25% and very preferably between 3% and 20%.

Advantageously, the proportion by weight of metal, with respect to the total weight of the adsorbent, is generally of between 1% and 60%, preferably between 2% and 40%, in a preferred way between 5% and 30%, very preferably between 5% and 20%.

The residence time in the adsorption section is generally of between 1 and 180 minutes.

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).

Steam cracking stage h) (optional)

The hydrocarbon effluent resulting from the separation stage c), or at least one of the two liquid hydrocarbon streams resulting from the optional stage f), can be sent, completely or partly, to a steam cracking stage h).

Advantageously, the gaseous effluent(s) resulting from the separation stage c) and/or the fractionation stage f) and containing ethane, propane and butane can also be sent, completely or partly, to the steam cracking stage h).

Said steam cracking stage h) 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 stage h) and after the separation stage c) (or the fractionation stage f)). The amount of water introduced, advantageously in the form of steam, is advantageously of between 0.3 and 3.0 kg of water per kg of hydrocarbon compounds at the inlet of stage h). Preferably, the optional stage h) is carried out in several pyrolysis furnaces in parallel, so as to adapt the operating conditions to the various streams feeding stage h), in particular resulting from

stage f), 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 the cracking of the hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C.

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 stage h) comprises the steam cracking furnaces but also the substages associated with the steam cracking which are well known to a person skilled in the art. These substages can in particular comprise heat exchangers, columns and catalytic reactors and recyclings 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 fraction comprising pyrolysis oil. 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 (C_2 cut) and a cut rich in propylene (C_3 cut) and optionally a cut rich in butenes (C_4 cut). The catalytic reactors make it possible in particular to carry out hydrogenations of the C_2, C_3, indeed even C_4, 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 stage h) makes it possible to obtain at least one effluent containing olefins comprising 2, 3 and/or 4 carbon atoms (that is to say C_2, C_3 and/or C_4 olefins), at satisfactory contents, in particular of greater than or equal to 30% by weight, in particular 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, with respect to the weight of the steam cracking effluent under consideration. Said C_2, C_3 and C_4 olefins can subsequently be advantageously used as polyolefin monomers.

According to a preferred embodiment of the invention, the process for the treatment of a feedstock comprising a plastics pyrolysis oil preferably comprises the linking together of the following stages, and preferably in the order given:

- hydrotreating stage b), separation/scrubbing stage c), stage d) of separation of the H_2S with recycling of the H_2S in stage b), and stage e) of separation of the NH_3

- hydrogenation stage a), hydrotreating stage b), separation/scrubbing stage c), stage d) of separation of the H_2S with recycling of the H_2S in stage a) and/or b), and stage e) of separation of the NH_3
- hydrogenation stage a), hydrotreating stage b), separation/scrubbing stage c), stage d) of separation of the H_2S with recycling of the H_2S in stage a) and/or b), stage e) of separation of the NH_3 and fractionation stage f)
- hydrogenation stage a), hydrotreating stage b), separation/scrubbing stage c), stage d) of separation of the H_2S with recycling of the H_2S in stage a) and/or b), stage e) of separation of the NH_3 and fractionation stage f)

and introduction of the hydrocarbon cut comprising compounds having a boiling point of greater than 175°C at the hydrocracking stage g), the hydrocracked effluent being recycled in stage c).

All the embodiments can comprise and preferably consist of, in addition, a pretreatment stage a0).

All the embodiments can comprise and preferably consist of, in addition, a steam cracking stage h).

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 a person 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	**Method**
Density @15°C	ASTM D4052
Sulfur Content	ISO 20846
Nitrogen Content	ASTM D4629
Acid Number	ASTM D664
Bromine Number	ASTM D1159
Content of Diolefins from the 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
Chloride Content	ASTM D7536
Content of Metals:	ASTM D5185
P	
Fe	
Si	
Na	
B	
Simulated distillation	ASTM D2887

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

LIST OF THE FIGURES

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

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

- a stage a) of hydrogenation (optional) of a hydrocarbon feedstock 1 resulting from the pyrolysis of plastics in the presence of a hydrogen-rich gas 2 and optionally of an amine contributed by the stream 3 and optionally of a sulfiding agent contributed by the stream 4 (in particular at the start of the cycle);
- a hydrotreating stage b) fed with the hydrocarbon effluent 5 resulting from the hydrogenation stage a), if present, and with a stream of a hydrogen-rich gas 6;
- a separation stage c) fed with the effluent 7 resulting from the hydrotreating stage b) and in the presence of an aqueous solution 10 in order to obtain at least a gaseous effluent 11, a first aqueous effluent 12 containing H_2S, HCl and NH_3 and a hydrocarbon effluent 13;
- a stage d) of separation of the H_2S contained in the first aqueous effluent 12, preferably by stripping with a stream containing steam 19, making it possible to obtain a gas phase containing the H_2S 20 and a second aqueous effluent 21, said gas phase containing the H_2S being at least partly recycled upstream of stage a) and/or stage b), preferably upstream of stage a), when it is present. This recycling of the phase containing the H_2S 20 makes it possible to keep the catalysts of stages a) and/or b) in the form of sulfides and thus to decrease the contribution of sulfiding agent 4;

- a stage e) of separation of the NH_3 contained in the second aqueous effluent 21, preferably by stripping with a stream containing steam 19, making it possible to obtain a gas phase containing NH_3 22 and a third aqueous effluent 23.

Figure 2 represents the diagram of another specific embodiment of the process of the present invention which is based on the diagram of Figure 1. This diagram comprises a stage c) carried out in two stages, then a fractionation stage f) and a hydrocracking stage g) in addition.

The hydrogenation stage a) and the hydrotreating stage b) are carried out as described in Figure 1. The separation stage c), carried out in two stages, comprises in particular:

- a stage c1) of separation of the hydrotreated effluent 7 carried out at high pressure and high temperature (HHPS), in order to obtain at least a gaseous effluent 8 and a liquid effluent 9, a part 9a of which can be recycled upstream of stage a) or upstream of stage b) (not displayed),
- a separation stage c2) carried out at high pressure and low temperature (CHPS) and fed with the gaseous effluent 8 and the other part of the liquid effluent 9b resulting from stage c1) and an aqueous solution 10, making it possible to obtain at least a gaseous effluent 11 comprising hydrogen, an aqueous effluent 12 containing dissolved salts and dissolved H_2S and NH_3, and a hydrocarbon effluent 13.

Stage d) of separation of the H_2S and stage e) of separation of the NH_3 are carried out as described in Figure 1. The recycling of the phase containing the H_2S 20 is carried out in the same way. It can also, at least partly, be recycled in the hydrocracking stage g).

Optionally, a stage f) of fractionation of the hydrocarbon effluent 13 is carried out which makes it possible to obtain at least a gaseous effluent 14, a first hydrocarbon cut 15 comprising compounds having a boiling point of less than or equal to 175°C (naphtha cut) and a second hydrocarbon cut 16 comprising compounds having a boiling point of greater than 175°C (middle distillates cut).

On conclusion of stage f), a part of the first hydrocarbon cut 15 comprising compounds having a boiling point of less than or equal to 175°C can be sent to a steam cracking process (not represented). Another part of the first hydrocarbon cut 15 can feed the hydrogenation stage a) and/or the hydrotreating stage b) (recycling not represented).

In Figure 2, at least a part of the second hydrocarbon cut 16 comprising compounds having a boiling point of greater than 175°C resulting from stage f) feeds a hydrocracking stage g), which is carried out in at least one fixed-bed reactor comprising at least one hydrocracking catalyst and is fed with hydrogen 17. The hydrocracked effluent 18 can be recycled between the separation stages c1) and c2) or also upstream of the separation stage c) (not represented).

Instead of injecting the amine stream 3 at the inlet of the hydrogenation stage a), it is possible to inject it at the inlet of the hydrotreating stage b), at the inlet of the separation stage c), at the inlet of the hydrocracking stage g), when it is present, or also not to inject it, depending on the characteristics of the feedstock.

Only the main stages, with the main streams, are represented in Figures 1 and 2, in order to make it possible for the invention to be better understood. It is clearly understood that all the items of equipment required for the operation are present (drums, pumps, exchangers, ovens/furnaces, columns, and the like), even if not represented. It is also understood that gas streams rich in hydrogen (supply or recycle), 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 a person 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 1 treated in the process with a flow rate of 10 000 kg/h (10 T/h) is a plastics pyrolysis oil (that is to say, comprising 100% by weight of said plastics pyrolysis oil) exhibiting the characteristics indicated in Table 2.

Table 2: Characteristics of the feedstock

Description /	**Method**	**Unit**	**Pyrolysis Oil**
Density @15°C	ASTM D4052	g/cm^3	0.845
Sulfur Content	ISO 20846	ppm by weight	170
Nitrogen Content	ASTM D4629	ppm by weight	2264
Acid Number	ASTM D664	mg KOH/g	3.95
Bromine Number	ASTM D1159	g Br_2/100 g	90
Content of Diolefins from the maleic anhydride value	MAV method(1)	% by weight	36
Content of Elemental Oxygen	ASTM D5622	% by weight	1.0
Content of Paraffins	UOP990-11	% by weight	19
Content of Naphthenes	UOP990-11	% by weight	7
Content of Olefins	UOP990-11	% by weight	31
Content of Aromatics	UOP990-11	% by weight	43
Content of Halogens	ASTM D7359	ppm by weight	400
Content of Asphaltenes	IFP 9313	ppm by weight	380
Content of Metals	ASTM D5185		
P		ppm by weight	46
Fe		ppm by weight	3
Si		ppm by weight	130
Na		ppm by weight	2.5
B		ppm by weight	5
As		ppb by weight	200
Hg		ppb by weight	20
Simulated Distillation	ASTM D2887		
0%		°C	45
10%		°C	94
30%		°C	135
50%		°C	180
70%		°C	250
90%		°C	394
100%		°C	550

(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

The feedstock 1 is subjected to a hydrogenation stage a) carried out in a fixed-bed reactor and in the presence of hydrogen 2 and of a hydrogenation catalyst of NiMo-on-alumina type, under the conditions indicated in Table 3.

Table 3: Conditions of the hydrogenation stage a)

Reactor inlet temperature	°C	290
Reactor outlet temperature	°C	320
Average temperature (WABT)	°C	305
Hydrogen partial pressure	MPa abs.	6.7
H_2/HC (hydrogen coverage by volume, with respect 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 3 correspond to conditions at the beginning of the cycle and the average temperature (WABT) is increased by 1°C per month so as to compensate for the catalytic deactivation.
On conclusion of the hydrogenation stage a), the degrees of conversion (= (initial concentration - final concentration)/initial concentration) observed are indicated in Table 4.

Table 4: Conversions of the entities during the hydrogenation stage a)

Degree of conversion of the diolefins	%	> 60
Degree of conversion of the olefins	%	> 60
Retention of silicon	%	> 75

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

Table 5: Conditions of the hydrotreating stage b)

Hydrotreating average temperature (WABT)	°C	325
Hydrogen partial pressure	MPa abs.	6.5
H_2/HC (hydrogen coverage by volume, with respect 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 beginning of the cycle and the average temperature (WABT) is increased by 1°C per month so as to compensate for the catalytic deactivation.

The effluent 7 resulting from the hydrotreating stage b) is subjected to a separation stage c): a stream of water 10 is injected into the effluent resulting from the hydrotreating stage b); the mixture is subsequently treated in a column for scrubbing sour gases and knockout drums, in order to obtain a gas fraction and a liquid effluent. The yields of the various fractions obtained after separation are shown in Table 6 (the yields correspond to the ratios of the amounts by weight of the various products obtained, with respect to the weight of feedstock upstream of stage a), expressed as percentage and denoted % w/w).

Table 6: Yields of the various products obtained after separation

Gas fraction (NH_3 + H_2S + H_2O + C_1-C_4)	% w/w	2.42
Liquid fraction	% w/w	99.31

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

The pyrolysis oil feedstock contains very little sulfur (170 ppm by weight). This sulfur, which exists in the form of sulfur-containing molecules, is hydrogenated in the reaction section and is converted into H_2S. This H_2S, in the form of a partial H_2S pressure (pH_2Sp) in the reactor, contributes to the maintenance of the sulfide phase of the NiMo-on-alumina catalysts. Nevertheless, the pH_2Sp obtained with this content of sulfur-containing compounds in the feedstock (170 ppm by weight) is insufficient to keep the catalysts in the sulfide phase throughout the cycle. This results in a rapid deactivation of the activity of the catalyst if nothing is done. It is thus advisable to add H_2S to the reaction system in order to achieve a

sufficient pH_2Sp. 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 pH_2Sp to keep the catalysts in sulfide form. This way of operating causes a high consumption of DMDS harmful to the economics of the process.

Another way, forming the subject-matter of the invention, is to recover the H_2S which is discharged in the aqueous effluent using a twofold stripping of this aqueous effluent and to reinject this H_2S at the inlet of the unit by dissolution in the pyrolysis oil feedstock.

The injection of DMDS and/or the recycling of H_2S at the inlet of the unit can serve both to maintain a sufficient pH_2Sp in the reaction system but also can serve to neutralize all the NH_3 resulting from the hydrogenation of the nitrogen-containing molecules. This is because the H_2S reacts with the NH_3 to form ammonium sulfides which will be virtually completely scrubbed out and transferred into the aqueous effluent (stream 12), making it possible to free the gas stream at the top outlet of the stabilization column from the presence of ammonia (stream 11). This gas stream, freed from the presence of ammonia, can thus be sent directly to the steam cracker in order to maximize the production of olefins.

The advantage of recycling an H_2S stream in comparison with injecting DMDS, whether in the context of maintaining a sufficient pH_2Sp or in the case of delivering a gas stream relieved of its ammonia, is thus to save on the amount of DMDS throughout the cycle.

Four operating cases are shown in Table 7.

Case 1: Simple stripping of sour water and injection of DMDS only in order to maintain a pH_2Sp sufficient to keep the catalysts in the sulfide phase.

Case 2: Twofold stripping of sour water in order to recycle, at the inlet of the unit, a stream predominant in H_2S resulting from the top of the first stripping column only in order to maintain a pH_2Sp sufficient to keep the catalysts in the sulfide phase. This case is in accordance with the invention.

Case 3: Simple stripping of sour water and injection of DMDS in order to maintain a pH_2Sp sufficient to keep the catalysts in the sulfide phase and also in order to neutralize all the NH_3 and to deliver an NH_3-free gas stream.

Case 4: Twofold stripping of sour water in order to recycle, at the inlet of the unit, a stream predominant in H_2S resulting from the top of the first stripping column in order to maintain a pH_2Sp sufficient to keep the catalysts in the sulfide phase and also in order to neutralize all the NH_3 and to deliver an NH_3-free gas stream. This case is in accordance with the invention.

It may be observed that the invention makes it possible to save 19 kg/h of DMDS when it is a matter of maintaining a minimum pH_2Sp for keeping the catalysts in sulfide form.

It may also be observed that the invention makes possible an even greater saving, namely 65 kg/h (75 – 10 = 65 kg/h) of DMDS saved for delivering an ammonia-free gas phase.

Table 7: Operating case

		Case 1 Simple stripping of sour water and minimum pH_2Sp	**Case 2** Twofold stripping of sour water and minimum pH_2Sp	**Case 3** Simple stripping of sour water and NH_3-free gas stream	**Case 4** Twofold stripping of sour water and NH_3-free gas stream
pH_2Sp at the outlet of the HDT reactor	bar a	0.02 (0.002 MPa)	0.02 (0.002 MPa)	0.21 (0.021 MPa)	0.21 (0.021 MPa)
Flow rate for injection of the DMDS	kg/h	19	0	75	10
DMDS saving	kg/h	-	**19**	-	**65**
Operating conditions of the stabilization column					
Pressure top of column	barg	7.1 (0.71 MPa)			
Pressure bottom of column	barg	7.3 (0.73 MPa)			
Temperature feedstock inlet	°C	160			
Number of theoretical plates		10			
Thermal flux of the reboiler	Gcal/h	0.55			
Operating conditions of the H_2S stripping column					
Pressure top of column	barg	N/A	9 (0.9 MPa)	N/A	9 (0.9 MPa)
Pressure bottom of column	barg		9.1 (0.91 MPa)		9.1 (0.91 MPa)
Temperature feedstock inlet	°C		135		130
Number of theoretical plates	-		12		12

Stripping steam flow rate	kg/h		285		303
Operating conditions of the NH_3 stripping column					
Pressure top of column	barg	N/A	2.4 (0.24 MPa)	N/A	2.4 (0.24 MPa)
Pressure bottom of column	barg		2.6 (0.26 MPa)		2.6 (0.26 MPa)
Temperature feedstock inlet	°C		124		126
Number of theoretical plates	-		15		15
Stripping steam flow rate	kg/h		535		538
Operating conditions of the simple stripping column (H_2S & NH_3)					
Pressure top of column	barg	2.4 (0.24 MPa)	N/A	2.4 (0.24 MPa)	N/A
Pressure bottom of column	barg	2.5 (0.25 MPa)		2.5 (0.25 MPa)	
Temperature feedstock inlet	°C	94		93	
Number of theoretical plates	-	15		15	
Stripping steam flow rate	kg/h	435		450	
Flow rate of the top gas of the stabilization column	kg/h	177	169	179	153
Composition of the top gas of the stabilization column					
H_2	mol%	29.3	31.7	26.4	33.7
H_2S	mol%	**NIL**	0.2	1.8	2.1
NH_3	mol%	9.6	9.8	**NIL**	**NIL**
H_2O	mol%	1.4	1.4	1.4	1.4
C_1	mol%	33.8	29.9	46.7	35.6
C_2	mol%	6.9	7.3	6.8	7.9
C_3	mol%	3.9	4.0	3.7	4.4
C_4	mol%	10.7	11.1	10.1	11.9
C_5+	mol%	4.5	4.4	3.1	3.1
Flow rate of the top H_2S-rich gas from the H_2S stripping column	kg/h	N/A	14	N/A	44
Composition of the top H_2S-rich gas from the H_2S stripping column					
H_2S	mol%	N/A	92.2	N/A	92.2
NH_3	mol%		0.05		0.07

H_2O	mol%		7.74		7.72
Flow rate of the top sour gas from the sour water stripping column	kg/h	40	22	103	44
Composition of the top sour gas from the NH_3 stripping (or simple stripping) column					
H_2S	mol%	24.5	2.7	32.7	3.0
NH_3	mol%	44.3	66.1	35.7	65.7
H_2O	mol%	31.2	31.3	31.6	31.2
Stripped water flow rate	kg/h	2553	2996	2551	3031
Composition of the stripped water					
H_2O	% by weight	99.9	99.9	99.9	99.9
NH_3	ppm by weight	< 30	< 30	< 30	< 30
H_2S	ppm by weight	< 5	< 5	< 5	< 5
Hydrocarbon	ppm by weight	Traces	Traces	Traces	Traces

CLAIMS

1. Process for the treatment of a feedstock comprising a plastics pyrolysis oil, comprising:

a) optionally a hydrogenation stage 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 and a gas stream comprising hydrogen, said hydrogenation reaction section being employed 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,

b) a hydrotreating stage carried out in a hydrotreating reaction section comprising at least one hydrotreating catalyst, said hydrotreating reaction section being fed at least with the feedstock or said hydrogenated effluent resulting from stage a) and a gas stream comprising hydrogen, said hydrotreating reaction section being employed 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,

c) a separation stage, fed with the hydrotreated effluent resulting from stage b) and optionally with the hydrocracked effluent resulting from stage g) and an aqueous solution, in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent,

d) a stage of separation of the H_2S contained in the first aqueous effluent, in order to obtain a gas phase containing the H_2S and a second aqueous effluent, said gas phase containing the H_2S being optionally, at least partly, recycled upstream of stage a) and/or stage b) and/or stage g),

e) a stage of separation of the NH_3 contained in the second aqueous effluent, in order to obtain a gas phase containing NH_3 and a third aqueous effluent, said gas phase containing NH_3 being optionally, at least in part, recycled upstream of stage a) and/or stage b) and/or stage g),

f) optionally a stage of fractionation of all or part of the hydrocarbon effluent resulting from stage c), in order to obtain at least a gaseous effluent and at least a first hydrocarbon cut comprising compounds having a boiling point of less than or equal to 175°C and a second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C,

g) optionally, a hydrocracking stage 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 resulting from stage c) and/or with at least a part of the second hydrocarbon cut comprising compounds having a boiling point of greater than 175°C resulting from stage f) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed 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.

2. Process according to the preceding claim, in which said gas phase containing the H_2S resulting from stage d) is at least partly recycled upstream of stage a) and/or stage b) and/or stage g).

3. Process according to either of the preceding claims, comprising the hydrogenation stage a).

4. Process according to one of the preceding claims, comprising the fractionation stage f).

5. Process according to one of the preceding claims, comprising the hydrocracking stage g).

6. Process according to one of the preceding claims, in which stage d) of separation of the H_2S contained in the first aqueous effluent is carried out by stripping said effluent with a stream containing steam at a pressure of between 0.5 and 1 MPa and a temperature of between 80 and 150°C.

7. Process according to one of the preceding claims, in which stage e) of separation of the NH_3 contained in the second aqueous effluent is carried out by stripping said effluent with a stream containing steam at a pressure of between 0.1 and 0.5 MPa and a temperature of between 80 and 150°C.

8. Process according to one of the preceding claims, in which the separation stage c) comprises the following stages:

c1) a separation stage, fed with the hydrotreated effluent resulting from stage b), said stage being carried out at a temperature of between 200 and 450°C and at a pressure substantially identical to the pressure of stage b), in order to obtain at least a gaseous effluent and a liquid effluent, a part of which is optionally recycled upstream of stage a) and/or of stage b),

c2) a separation stage, fed with the gaseous effluent resulting from stage c1) and another part of the liquid effluent resulting from stage c1) and an aqueous solution, said stage being carried out at a temperature of between 20 and less than 200°C and at a pressure

substantially identical to or less than the pressure of stage b), in order to obtain at least a gaseous effluent, a first aqueous effluent and a hydrocarbon effluent.

9. Process according to one of the preceding claims, comprising at least one stage a0) of pretreatment of the feedstock comprising a plastics pyrolysis oil, optionally as a mixture with the hydrocarbon effluent resulting from stage c), said pretreatment stage being carried out upstream of stage a) and/or upstream of stage b), and comprises a filtration stage and/or a centrifugation stage and/or an electrostatic separation stage and/or a stage of scrubbing by means of an aqueous solution and/or an adsorption stage and/or a selective hydrogenation stage.

10. Process according to one of the preceding claims, in which the hydrocarbon effluent resulting from the separation stage c), or at least one of the two liquid hydrocarbon cuts resulting from stage f), is sent, completely or partly, to a steam cracking stage h) 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.

11. Process according to one of the preceding claims, in which said gas phase containing the NH_3 resulting from stage e) is at least partly recycled upstream of stage a) and/or stage b) and/or stage g).

12. Process according to one of the preceding claims, in which a stream containing a nitrogen compound and/or a sulfur compound is injected upstream of stage a) and/or upstream of stage b).

13. Process according to one of the preceding claims, in which said hydrogenation catalyst comprises a support chosen from alumina, silica, silicas-aluminas, magnesia, clays and their mixtures 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.

14. Process according to one of the preceding claims, in which said hydrotreating catalyst comprises a support chosen from the group consisting of alumina, silica, silicas-aluminas, magnesia, clays and their mixtures and a hydro-dehydrogenating function comprising at least one element from group VIII and/or at least one element from group VIB.

15. Process according to one of the preceding claims, which additionally comprises a second hydrocracking stage g') 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 resulting from the first hydrocracking stage g) and a gas stream comprising hydrogen, said hydrocracking reaction section being employed at a 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.

16. Process according to one of the preceding claims, in which said hydrocracking catalyst comprises a support chosen from halogenated aluminas, combinations of boron and aluminium oxides, amorphous silicas-aluminas and zeolites and a hydro-dehydrogenating function comprising at least one metal from group VIB chosen from chromium, molybdenum and tungsten, alone or as a mixture, and/or at least one metal from group VIII chosen from iron, cobalt, nickel, ruthenium, rhodium, palladium and platinum.

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

18. Product according to Claim 17, which comprises, with respect 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.

Figure 1

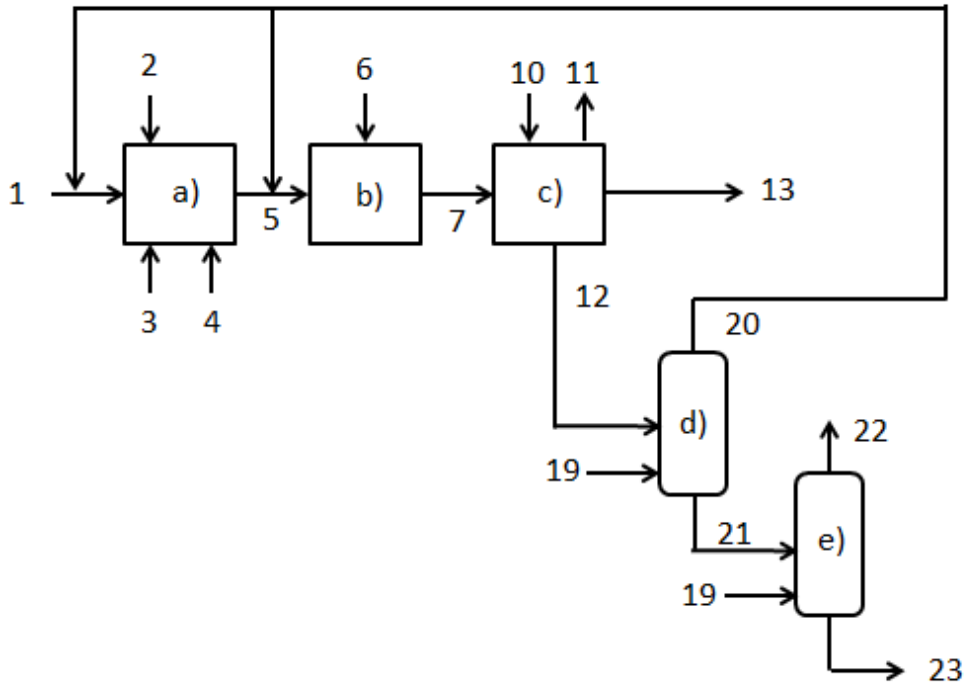

Figure 2