

PROCESS FOR HYDROTREATMENT AND HYDROISOMERIZATION OF FEEDSTOCKS OBTAINED FROM A RENEWABLE SOURCE IMPLEMENTING A MODIFIED ZEOLITE

Field of the Invention

In an international context marked by the rapid growth of fuel requirements, in particular gas oil and kerosene bases in the European Community, the search for new sources of renewable energy that can be integrated into the traditional arrangement of the refining and production of fuels constitutes a major venture.

In this regard, there has been a very sharp resurgence, in recent years, of interest in integration into the process for refining new products of plant origin, obtained from the conversion of the lignocellulosic biomass or obtained from the production of vegetable oils or animal fats, due to the increase in the cost of fossil fuels. Likewise, the traditional biofuels (ethanol or methyl esters of vegetable oils, primarily) have acquired an actual status of a supplement to petroleum-type fuels in the fuel pools. In addition, the processes that are now known that use vegetable oils or animal fats are at the origin of CO₂ emissions, known for these negative effects on the environment. A better use of these bio resources, such as, for example, their integration into the fuel pool, would therefore offer a certain advantage.

The high demand for gas oil and kerosene fuels, coupled with the importance of concerns linked to the environment, reinforces the advantage of using feedstocks obtained from renewable sources. Among these feedstocks, it is possible to cite, for example, vegetable oils, animal fats that are raw or that have been pretreated, as well as mixtures of such feedstocks. These feedstocks contain chemical structures such as triglycerides or esters or fatty acids, whereby the structure and the length of the hydrocarbon chain of the latter are compatible with the hydrocarbons that are present in the gas oils and kerosene.

One possible method is the catalytic transformation of the feedstock that is obtained from the renewable source of paraffinic fuel from which oxygen is removed in the presence of hydrogen (hydrotreatment). Numerous metal or sulfur catalysts are known for being active for this type of reaction.

These processes for hydrotreatment of the feedstock obtained from a renewable source are already well known and are described in numerous patents. It is possible to cite, for example, the patents: US 4,992,605, US 5,705,722, EP 1,681,337 and EP 1,741,768.

The use of solids based on transition metal sulfides makes possible the production of paraffins from the ester-type molecule according to two reaction methods:

- The hydrodeoxygenation leading to the formation of water by consumption of hydrogen and to the formation of hydrocarbons of the carbon number (Cn) that is equal to that of the starting fatty acid chains,
- The decarboxylation/decarbonylation leading to the formation of carbon oxides (carbon monoxide and carbon dioxide: CO and CO₂) and to the formation of hydrocarbons, having one carbon less (Cn-1) relative to the starting fatty acid chains

The liquid effluent that is obtained from these hydrotreatment processes essentially consists of n-paraffins that can be incorporated in the gas oil and kerosene pool. So as to improve the properties under cold conditions of this hydrotreated liquid effluent, a hydroisomerization stage is necessary for transforming the n-paraffins into branched paraffins exhibiting better properties under cold conditions.

The patent application EP 1 741 768 describes, for example, a process that comprises hydrotreatment followed by a hydroisomerization stage so as to improve the properties under cold conditions of the linear paraffins that are obtained. The catalysts that are used in the hydroisomerization stage are bifunctional catalysts and consist of a metal active phase that comprises a metal of group VIII that is selected from among palladium, platinum and nickel, dispersed on a molecular sieve-type acid substrate that is selected from among SAPO-11, SAPO-41, ZSM-22, ferrierite or ZSM-23, whereby said process operates at a temperature of between 200 and 500°C, and at a pressure of between 2 and 15 MPa. Nevertheless, the use of this type of solid brings about a loss in yield of middle distillates.

The research work carried out by the applicant on the modification of numerous zeolites and crystallized microporous solids and on the hydrogenating active phases has led to the discovery that, surprisingly enough, a catalyst for hydroisomerization of

paraffinic hydrocarbon feedstocks and in particular obtained from the hydrotreatment of feedstocks obtained from a renewable source, comprising an active phase that contains at least one hydro-dehydrogenating element that is selected from among the elements of group VIB and group VIII, and a substrate that comprises at least one zeolite that exhibits at least one series of channels whose opening is defined by a ring with 8 oxygen atoms, whereby said zeolite is modified by a particular modification process, made it possible to obtain a higher activity, i.e., a higher level of conversion, while making it possible to obtain an improved yield of middle distillates (jet fuels and gas oils), the hydroisomerization stage being implemented in a process for treatment of feedstocks obtained from a renewable source comprising a hydrotreatment stage upstream from said hydroisomerization stage.

The modification of zeolite by deposition of compounds containing at least one molecular compound containing at least one silicon atom has been very widely studied in the past. Moreover, it is possible to cite the patent US 4,402,867 that describes a method for preparation of a zeolite-based catalyst that comprises a stage consisting in depositing, in aqueous phase, at least 0.3% by weight of amorphous silica inside the pores of the zeolite. The patent US 4,996,034 describes a process for substitution of aluminum atoms that are present in a zeolitic framework by silicon atoms, whereby said process is carried out in one stage in aqueous medium using fluorosilicate salts. The patent US 4,451,572 describes the preparation of a zeolitic catalyst that comprises a stage for deposition of organosilicic materials in vapor phase or in liquid phase, whereby the targeted zeolites are zeolites with wide pores, in particular the Y zeolite.

One objective of the invention is therefore to provide a process for treatment of feedstocks obtained from a renewable source implementing – in one hydroisomerization stage downstream from a hydrotreatment stage – a hydroisomerization catalyst that comprises a modified zeolite-based substrate that makes it possible to obtain high yields of gas oil and kerosene bases.

Another objective of the invention is to provide a process for treatment of feedstocks obtained from a renewable source implementing – in one hydroisomerization stage downstream from a hydrotreatment stage – a catalyst that comprises as substrate a modified zeolite that makes it possible to reduce the 150°C- light fraction production.

Object of the Invention

More specifically, the invention relates to a process for treatment of feedstocks obtained from a renewable source and comprising the following stages:

a) Hydrotreatment of said feedstock in the presence of a fixed-bed catalyst that comprises a hydro-dehydrogenating function comprising at least one metal of group VIII and/or group VIB, taken by itself or in a mixture, and a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals, whereby said hydrotreatment stage operates at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 h⁻¹ and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock,

b) Separation, starting from the effluent that is obtained from stage a), of hydrogen, gases, and at least one hydrocarbon base,

c) Hydroisomerization of at least a portion of said hydrocarbon base that is obtained from stage b) in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and group VIII of the periodic table, taken by itself or in a mixture, and a substrate that comprises at least one zeolite that has at least one series of channels whose opening is defined by a ring with 8 oxygen atoms, modified by a') at least one stage for introducing at least one alkaline cation that belongs to group IA or IIA of the periodic table, b') a stage for treatment of said zeolite in the presence of at least one molecular compound that contains at least one silicon atom, c') at least one stage of partial exchange of said alkaline cations by NH₄⁺ cations, and d') at least one heat treatment stage, whereby said hydroisomerization stage is carried out at a temperature of between 150 and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³/m³ of feedstock,

d) Separation, starting from the effluent that is obtained from stage c), of hydrogen, gases, and at least one gas oil base and one kerosene base.

Detailed Description of the Invention

This invention is particularly devoted to the preparation of gas oil and kerosene fuel bases corresponding to new environmental standards, starting from feedstocks obtained from renewable sources.

The feedstocks that are obtained from renewable sources used in this invention are advantageously selected from among the oils and fats of plant or animal origin, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters. The vegetable oils can advantageously be raw or refined, totally or partially, and obtained from the following plants: canola, sunflower, soybean, palm, palm-kernel, olive, coconut, and jatropha, whereby this list is not exhaustive. The oils of algae or fish are also relevant. Animal fats are advantageously selected from among lard or fats composed of waste from the food industry or obtained from catering industries.

These feedstocks essentially contain chemical structures of the triglyceride type that one skilled in the art also knows under the name fatty acid triesters as well as free fatty acids. A fatty acid triester is thus composed of three chains of fatty acids. These fatty acid chains in triester form or in free fatty acid form have a number of unsaturations per chain, also called a number of carbon-carbon double bonds per chain, generally encompassed between 0 and 3 but that can be higher in particular for the oils that are obtained from algae that generally have a number of unsaturations per chain of 5 to 6.

The molecules that are present in the feedstocks that are obtained from renewable sources used in this invention therefore have a number of unsaturations, expressed per triglyceride molecule, advantageously between 0 and 18. In these feedstocks, the unsaturation level, expressed by number of unsaturations per hydrocarbon fatty chain, is advantageously between 0 and 6.

The feedstocks that are obtained from renewable sources generally also comprise various impurities and in particular heteroatoms such as nitrogen. The nitrogen contents in the vegetable oils are generally between approximately 1 ppm and 100 ppm by weight according to their nature. They can reach up to 1% by weight in particular feedstocks.

Prior to stage a) of the process according to the invention, the feedstock can advantageously undergo a stage for pretreatment or pre-refining so as to eliminate, by a suitable treatment, contaminants such as metals, like the alkaline compounds, for example, on ion-exchange resins, alkaline-earths, and phosphorus. Suitable treatments can be, for example, heat treatments and/or chemical treatments that are well known to one skilled in the art.

According to stage a) of the process according to the invention, the feedstock, optionally pretreated, is brought into contact with a fixed-bed catalyst comprising a hydro-dehydrogenating function that comprises at least one metal of group VIII and/or group VIB, taken by itself or in a mixture and a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals, whereby said hydrotreatment stage operates at a temperature of between 200 and 450°C, preferably between 220 and 350°C, in a preferred manner between 220 and 320°C, and in an even more preferred manner between 220 and 310°C. The pressure is between 1 MPa and 10 MPa, in a preferred manner between 1 MPa and 6 MPa, and in an even more preferred manner between 1 MPa and 4 MPa. The hourly volumetric flow rate is between 0.1 h⁻¹ and 10 h⁻¹. The feedstock is brought into contact with the catalyst in the presence of hydrogen. The total quantity of hydrogen mixed with the feedstock is such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock, and in a preferred manner between 150 and 750 Nm³ of hydrogen/m³ of feedstock.

In stage a) of the process according to the invention, the substrate of the catalyst that is implemented can also advantageously contain other compounds and, for example, oxides that are selected from the group that is formed by boron oxide, zirconia, titanium oxide, and phosphoric anhydride. The preferred substrate is an alumina substrate and in a very preferred manner η -, δ -, or γ -alumina.

Said catalyst is advantageously a catalyst that comprises metals of group VIII that are preferably selected from among nickel and cobalt, taken by itself or in a mixture, preferably combined with at least one metal of group VIB, preferably selected from among molybdenum and tungsten, taken by itself or in a mixture.

The content of metal oxides of group VIII and preferably of nickel oxide is advantageously between 0.5 and 10% by weight of nickel oxide (NiO) and preferably between 1 and 5% by weight of nickel oxide, and the content of metal oxides of group VIB and preferably of molybdenum trioxide is advantageously between 1 and 30% by weight of molybdenum oxide (MoO_3), preferably 5 to 25% by weight, the percentages being expressed in terms of % by weight relative to the total mass of the catalyst.

The total content of oxides of metals of groups VIB and VIII in the catalyst used in stage a) is advantageously between 5 and 40% by weight and preferably between 6 and 30% by weight relative to the total mass of the catalyst.

The ratio by weight that is expressed in terms of metal oxide between metal (or metals) of group VIB to metal (or metals) of group VIII is advantageously between 20 and 1 and in a preferred manner between 10 and 2.

Said catalyst that is used in stage a) of the process according to the invention is advantageously to be characterized by a strong hydrogenating power so as to orient as much as possible the selectivity of the reaction to a hydrogenation preserving the number of carbon atoms of the fatty chains, i.e., the hydrodeoxygenation method, so as to maximize the yield of hydrocarbons entering the field of distillation of kerosenes and/or gas oils. This is why the operation is performed in a preferred manner at a relatively low temperature. Maximizing the hydrogenating function also makes it possible to limit the reactions of polymerization and/or condensation leading to the formation of coke that would degrade the stability of the catalytic performances. Preferably, a catalyst of Ni or NiMo type is used.

Said catalyst that is used in stage a) for hydrotreatment of the process according to the invention can also advantageously contain a doping element that is selected from among phosphorus and boron, taken by themselves or in a mixture. Said doping element can be introduced into the matrix or preferably be deposited on the substrate. It is also possible to deposit silicon on the substrate by itself or with phosphorus and/or boron and/or fluorine.

The content by weight of oxide of said doping element is advantageously less than 20% and preferably less than 10%, and it is advantageously at least 0.001%.

The metals of the catalysts that are used in stage a) for hydrotreatment of the process according to the invention are sulfurized metals or metal phases and preferably sulfurized metals.

The scope of this invention would not be exceeded by using a single catalyst or several different catalysts simultaneously or successively in stage a) of the process according to the invention. This stage can be carried out industrially in one or more reactors with one or more catalytic beds and preferably with liquid downflow.

According to stage b) of the process according to the invention, the hydrotreated effluent that is obtained from stage a) is subjected at least partially, and preferably completely, to one or more separations. The object of this stage is to separate the gases from the liquid and in particular to recover the hydrogen-rich gases that can also contain gases such as CO and CO₂, and at least one liquid hydrocarbon base with a sulfur content that is less than 10 ppm by weight. The separation is carried out according to all separation methods that are known to one skilled in the art. The separation stage can advantageously be implemented by any method that is known to one skilled in the art, such as, for example, the combination of one or more high- and/or low-pressure separators, and/or distillation stages and/or high- and/or low-pressure stripping stages.

The water that is optionally formed during the stage a) for hydrotreatment of the process according to the invention can also advantageously be separated at least partially from the liquid hydrocarbon base. The separation stage b) can therefore advantageously be followed by an optional stage for elimination of at least a portion of the water and preferably all of the water.

The optional stage for water removal has as its object to eliminate at least partially the water that is produced during hydrotreatment reactions. Elimination of water is defined as the elimination of the water that is produced by hydrodeoxygenation (HDO) reactions. The more or less complete elimination of the water can be based on the tolerance to water of the hydroisomerization catalyst used in the subsequent stage c) of the process according to the invention. The elimination of the water can be carried out by any of the methods and techniques known to one skilled in the art, for example by drying, running it over a desiccant, flash, decanting, ...

According to stage c) of the process according to the invention, at least a portion and preferably all of the liquid hydrocarbon base obtained at the end of stage b) of the process according to the invention is hydroisomerized in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and of group VIII of the periodic table, taken by itself or in a mixture, and a substrate that comprises at least one zeolite that has at least one series of channels whose opening is defined by a ring with 8 oxygen atoms, whereby said zeolite is modified according to a particular process.

The Hydrogenating Phase

According to the invention, the catalyst that is implemented in stage c) for hydroisomerization of the process according to the invention comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIII and the metals of group VIB, taken by themselves or in a mixture.

Preferably, the elements of group VIII are selected from among iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, or platinum, taken by themselves or in a mixture.

In the case where the elements of group VIII are selected from among the noble metals of group VIII, the elements of group VIII are advantageously selected from among platinum and palladium, taken by themselves or in a mixture.

In the case where the elements of group VIII are selected from among the non-noble metals of group VIII, the elements of group VIII are advantageously selected from among iron, cobalt and nickel, taken by themselves or in a mixture.

Preferably, the elements of group VIB of the catalyst according to this invention are selected from among tungsten and molybdenum.

In the case where the catalyst comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, the metal content of group VIB is advantageously encompassed, in oxide equivalent, between 5 and 40% by weight relative to the total mass of said catalyst, in a preferred manner between 10 and 35% by weight and in a very preferred manner between 15 and 30% by weight, and the content of

non-noble metal of group VIII is advantageously encompassed, in oxide equivalent, between 0.5 and 10% by weight relative to the total mass of said catalyst, in a preferred manner between 1 and 8% by weight, and in a very preferred manner between 1.5 and 6% by weight.

In the case where said catalyst comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, said catalyst can also advantageously comprise at least one doping element that is selected from the group that consists of silicon, boron, and phosphorus, taken by itself or in a mixture, whereby the content of doping element is preferably between 0 and 20% by weight of oxide of the doping element, in a preferred manner between 0.1 and 15% by weight, in a very preferred manner between 0.1 and 10% by weight, and in a very preferred manner between 0.5 and 6% by weight relative to the total mass of the catalyst.

In the case where the hydrogenating function comprises an element of group VIII and an element of group VIB, the following metal combinations are preferred: nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, cobalt-tungsten, and in a very preferred manner: nickel-molybdenum, cobalt-molybdenum, and nickel-tungsten. It is also possible to use combinations of three metals, such as, for example, nickel-cobalt-molybdenum.

When a combination of metals of group VI and group VIII is used, the catalyst is then preferably used in a sulfurized form.

When the hydro-dehydrogenating element is a noble metal of group VIII, the catalyst preferably contains a content of noble metal of between 0.01 and 10% by weight, in an even more preferred manner 0.02 to 5% by weight relative to the total mass of said catalyst. The noble metal is preferably used in its reduced and non-sulfurized form.

It is advantageously also possible to use a catalyst that is based on reduced and non-sulfurized nickel. In this case, the content of metal in its oxide form is advantageously between 0.5 and 25% by weight relative to the finished catalyst. Preferably, the catalyst also contains, in addition to the reduced nickel, a metal of group IB and preferably copper, or a metal of group IVB and preferably tin in proportions such that the ratio by mass of the metal of group IB or IVB and nickel to the catalyst is advantageously between 0.03 and 1.

Said hydroisomerization catalyst that is used in stage c) of the process according to the invention comprises a substrate that comprises at least one modified zeolite and advantageously an oxide-type porous mineral matrix, whereby said substrate comprises and preferably consists of, preferably:

- 0.1 to 99.8% by weight, preferably 0.1 to 80% by weight, and in an even more preferred manner 0.1 to 70% by weight, and in a very preferred manner 0.1 to 50% by weight of modified zeolite according to the invention relative to the total mass of the catalyst,
- 0.2 to 99.9% by weight, preferably 20 to 99.9%, in a preferred manner 30 to 99.9% by weight, and in a very preferred manner 50 to 99.9% by weight relative to the total mass of catalyst, of at least one oxide-type porous mineral matrix.

The Zeolite According to the Invention

According to the invention, the zeolite that is contained in the substrate of the catalyst that is used in stage c) of the process according to the invention comprises at least one series of channels whose opening is defined by a ring with 8 oxygen atoms (8 MR) before being modified. Said zeolite is selected from among the zeolites that are defined in the classification "Atlas of Zeolite Structure Types," Ch. Baerlocher, L. B. McCusker, D. H. Olson, 6th Edition, Elsevier, 2007, Elsevier" that has at least one series of channels whose opening of pores is defined by a ring that contains 8 oxygen atoms.

According to one particular embodiment, the initially used zeolite, before being modified, can advantageously contain – in addition to at least one series of channels whose opening is defined by a ring with 8 oxygen atoms (8 MR) – at least one series of channels whose pore opening is defined by a ring that contains 10 oxygen atoms (10 MR) and/or at least one series of channels whose pore opening is defined by a ring that contains 12 oxygen atoms (12 MR).

The zeolite can advantageously contain at least one other element T, different from silicon and aluminum, being integrated in tetrahedral form in the framework of the zeolite. Preferably, said element T is selected from among iron, germanium, boron and titanium and represents a proportion by weight of between 2 and 30% of all of the

constituent atoms of the zeolitic framework other than the oxygen atoms. The zeolite then has an atomic ratio $(\text{Si}+\text{T})/\text{Al}$ of between 2 and 200, preferably between 3 and 100, and in a very preferred manner between 4 and 80, whereby T is defined as above.

Preferably, the zeolite that is contained in the substrate of the catalyst that is used in stage c) of the process according to the invention is selected from among the zeolites Y, ZSM-48, ZBM-30, IZM-1 and COK-7, taken by themselves or in a mixture. Preferably, the zeolite is selected from among the zeolites Y, ZSM-48, ZBM-30, IZM-1 and COK-7, taken by themselves or in a mixture. Very preferably, said zeolite is selected from among the zeolites Y, ZSM-48 and ZBM-30, whereby ZBM 30 is preferably synthesized with the organic structurant triethylenetetramine, taken by themselves or in a mixture.

The ZBM-30 zeolite is described in the patent EP-A-46 504, and the COK-7 zeolite is described in the patent application EP 1 702 888 A1 or FR 2 882 744 A1.

The IZM-1 zeolite is described in the patent application FR-A-2 911 866, and the ZSM 48 zeolite is described in Schlenker, J. L.; Rohrbaugh, W.J.; Chu, P.; Valoyocsik, E. W.; and Kokotailo, G. T. Title: The Framework Topology of ZSM-48: A High Silica Zeolite Reference: Zeolites, 5, 355-358 (1985) Material *ZSM-48."

In a more preferred manner, the initially used zeolite is an FAU zeolite that has a three-dimensional network of channels whose opening is defined by a ring with 12 oxygen atoms (12 MR), and in an even more preferred manner, the initial zeolite is the Y zeolite.

Preferably, said zeolite can advantageously be dealuminified in all of the known manners by one skilled in the art such that the atomic ratio of silicon to aluminum of the zeolite is between 2.5 and 200, preferably between 3 and 100, and even more preferably between 4 and 80. The atomic ratio of the silicon to aluminum Si/Al framework of the zeolite is measured by NMR of silicon and aluminum according to a method that is known to one skilled in the art.

The FAU-structural-type zeolite that has undergone one or more dealuminification stages and that has a three-dimensional network of channels whose opening is defined by a ring with 12 oxygen atoms (12 MR) is suitable for the implementation of the catalyst that is used in the process according to the invention.

Preferably, the initially used zeolite is a dealuminified FAU zeolite, and in a very preferred manner, the initial zeolite is the dealuminified Y zeolite.

Process for Modification of the Zeolite that is Contained in the Substrate of the Catalyst that is Used in the Process According to the Invention.

According to the invention, the zeolite that is contained in the substrate of the catalyst that is used in stage c) of the process according to the invention, initially exhibiting, before being modified, at least one series of channels whose opening is defined by a ring with 8 oxygen atoms (8 MR), is modified by a') a stage for introducing at least one alkaline cation that belongs to group IA or IIA of the periodic table, b') a stage for treatment of said zeolite in the presence of at least one molecular compound that contains at least one silicon atom, c') at least one partial exchange of alkaline cations by NH_4^+ cations, and d) at least one heat treatment stage.

Said initial zeolite is therefore modified according to a modification process that comprises at least one stage a') for introducing at least one alkaline cation that belongs to the groups IA and IIA of the periodic table, whereby said cation(s) is/are preferably selected from among the cations Na^+ , Li^+ , K^+ , Rb^+ , Cs^+ , Ba^{2+} and Ca^{2+} , and in a very preferred manner, said cation is the Na^+ cation. This stage can be carried out by any of the methods known to one skilled in the art, and preferably this stage is carried out by the so-called ion-exchange method.

At the end of stage a') of the modification process, the zeolite that is contained in the substrate of the catalyst used in stage c) of the process according to the invention is found in cationic form.

The process for modification of said zeolite next comprises a stage b') for treatment in the presence of at least one molecular compound that contains at least one silicon atom. This stage is called a stage for selecting said zeolite. In terms of this invention, "selecting" is defined as the neutralization of the acidity of each of the crystals of the cationic zeolite. The neutralization of the acidity can be done by any method that is known to one skilled in the art. The conventional methods generally use molecular compounds that contain atoms that can interact with the sites of the crystals of the zeolite.

The molecular compounds that are used within the scope of the invention are organic or inorganic molecular compounds that contain one or more silicon atom(s).

Also, according to treatment stage b'), the cationic zeolite that is prepared according to stage a') is subjected to a treatment stage in the presence of at least one molecular compound that contains at least one silicon atom. Said stage b') allows the deposition of a layer of said molecular compound that contains at least one silicon atom at the surface of the crystals of the zeolite that will be transformed after stage c') into a layer of amorphous silica on the surface of each of the crystals of the zeolite.

Preferably, the molecular compound that contains at least one silicon atom is selected from among the compounds of formulas Si-R_4 and $\text{Si}_2\text{-R}_6$, where R is selected from among hydrogen, an alkyl, aryl or acyl group, an alkoxy group ($\text{O-R}'$), a hydroxyl group ($-\text{OH}$), or a halogen, and preferably an alkoxy group ($\text{O-R}'$). Within the same molecule Si-R_4 or $\text{Si}_2\text{-R}_6$, the group R can advantageously be either identical or different. Preferably, the molecular compound is selected from among the compounds of formula Si_2H_6 or $\text{Si}(\text{C}_2\text{H}_5)_3(\text{CH}_3)$. Thus, the molecular compound that contains at least one silicon atom that is used in stage b) of the process according to the invention can advantageously be a compound such as silane, disilane, alkylsilane, alkoxy silane or siloxane.

Said molecular compound that is used for implementing stage b') according to the invention preferably comprises at most two silicon atoms per molecule.

In a very preferred manner, said molecular compound has a compound of general formula Si-(OR')_4 where R' is an alkyl, aryl or acyl group, preferably an alkyl group, and very preferably an ethyl group.

Very preferably, the molecular compound that contains at least one silicon atom is the molecular compound tetraethylorthosilicate (TEOS) of formula $\text{Si}(\text{OCH}_2\text{CH}_3)_4$.

Said stage b') of the process for modification that consists in treating the cationic zeolite that is exchanged according to stage a') in the presence of at least one molecular compound that contains at least one silicon atom is advantageously implemented by deposition of said compound on the inside and outside surfaces of the zeolite. It is possible to initiate a gas-phase deposition called a CVD ("Chemical Vapor Deposition") deposition or a liquid-phase deposition that is called a CLD ("Chemical Liquid

Deposition”) deposition by any of the methods that are known to one skilled in the art. In a very preferred manner, said stage b’) is implemented by initiating the deposition of said molecular compound that contains at least one liquid-phase silicon atom.

If stage b’) of the modification process is implemented by gas-phase deposition (CVD), it is advantageously implemented in a fixed-bed reactor. Prior to the gas-phase deposition reaction (CVD) in said fixed-bed reactor, the zeolite is preferably activated. The activation of the zeolite in the fixed-bed reactor is implemented under oxygen, in air, or under a cover gas, or under a mixture of air and inert gas or oxygen and inert gas. The temperature for activating the zeolite is advantageously between 100 and 600°C and very advantageously between 300 and 550°C. The molecular compound that contains at least one silicon atom that should be deposited on the outside surface of each of the crystals of the zeolite is sent into the vapor-phase reactor, whereby said molecular compound is diluted in a carrier gas that can be either hydrogen (H₂), or air, or argon (Ar), or helium (He), or else nitrogen (N₂); preferably, the carrier gas is an inert gas that is selected from among Ar, He and N₂. Said molecular compound that contains at least one silicon atom is deposited on the outside surface of said vapor-phase zeolite. To obtain a layer of amorphous silica of optimal quality on the outside surface of the zeolite at the end of stage c’), it is necessary to select the operating conditions properly for the deposition of the molecular compound that contains at least one silicon atom. In particular, the temperature of the zeolite bed during the deposition is preferably between 10 and 300°C, and very preferably between 50 and 200°C; the partial pressure, in the gas phase, of the molecular compound to be deposited on the outside surface of the zeolite is preferably between 0.001 and 0.5 bar, and very preferably between 0.01 and 0.2 bar; the duration of the deposition is preferably between 10 minutes and 10 hours, and very preferably between 30 minutes and 5 hours, and even more preferably between 1 and 3 hours.

If stage b’) of the modification process is carried out by liquid-phase deposition (CLD), it is advantageously carried out while being stirred. A CLD-phase deposition can be done either in aqueous medium or in an organic solvent. During impregnation in an aqueous medium of the molecular compound that contains at least one silicon atom, it may or may not be possible to add one or more surfactant(s) into the impregnation solution. The CLD deposition is well known to one skilled in the art (Chon et al., Studies

in Surface Science and Catalysis, Vol. 105, 2059-2065, 1997). In a preferred manner, said molecular compound that contains at least one silicon atom is deposited on the outside surface of said zeolite in an anhydrous organic solvent. The organic solvent is advantageously selected from among the saturated or unsaturated molecules containing 5 to 10 carbon atoms, and in a preferred manner 6 to 8 carbon atoms. To obtain a layer of amorphous silica of optimal quality on the outside surface of the zeolite at the end of stage c'), it is necessary to select the operating conditions properly for the deposition of the molecular compound that contains at least one silicon atom. In particular, the temperature of the organic solvent solution is preferably between 10 and 100°C, and very preferably between 30 and 90°C. The quantity of silica added to the solution of anhydrous solvent is advantageously between 0.0001 and 5% by weight, preferably between 0.0001 and 2% by weight, and in an even more preferred manner between 0.0005 and 1% by weight relative to the quantity of zeolite. The duration of the deposition is preferably between 5 minutes and 10 hours, preferably between 30 minutes and 5 hours, and even more preferably between 1 and 3 hours.

The process for modification of the zeolite next comprises a stage c') that corresponds to at least one partial exchange of alkaline cations that belong to the groups IA and IIA of the periodic table introduced during stage a') and preferably Na⁺ cations by NH₄⁺ cations. Partial exchange of alkaline cations, and preferably Na⁺ cations by NH₄⁺ cations, is defined as the exchange of 80 to 99%, in a preferred manner 85 to 98%, and in a more preferred manner 90 to 98% of the alkaline cations and preferably Na⁺ cations by NH₄⁺ cations. The quantity of alkaline cations remaining and preferably the quantity of Na⁺ cations remaining in the modified zeolite, relative to the quantity of NH₄⁺ cations initially present in the zeolite, is advantageously between 1 and 20%, preferably between 1.5 and 20%, in a preferred manner between 2 and 15%, and in a more preferred manner between 2 and 10%.

Preferably, for this stage, several ion exchange(s) are initiated with a solution that contains at least one ammonium salt that is selected from among the salts of chlorate, sulfate, nitrate, phosphate or acetate of ammonium, in such a way as to eliminate, at least partially, the alkaline cations and preferably the Na⁺ cations that are present in the zeolite. Preferably, the ammonium salt is ammonium nitrate NH₄NO₃.

Thus, preferably, the content of alkaline cations remaining and preferably Na^+ cations in the modified zeolite at the end of stage c') is preferably such that the alkaline cation/aluminum molar ratio and preferably the Na/Al molar ratio is between 0.2:1 and 0.01:1, preferably between 0.2:1 and 0.015:1, in a more preferred manner between 0.15:1 and 0.02:1, and in an even more preferred manner between 0.1:1 and 0.02:1.

The desired Na/Al ratio is obtained by adjusting the NH_4^+ concentration of the cationic exchange solution, the temperature of the cationic exchange, and the cationic exchange number. The concentration of the NH_4^+ solution in the solution advantageously varies between 0.01 and 12 mol/L, and preferably between 1 and 10 mol/L. The temperature of the exchange stage is advantageously between 20 and 100°C, preferably between 60 and 95°C, in a preferred manner between 60 and 90°C, and in a more preferred manner between 60 and 85°C, and in an even more preferred manner between 60 and 80°C. The cationic exchange number advantageously varies between 1 and 10 and preferably between 1 and 4.

Maintaining a controlled content of alkaline cations and preferably Na^+ cations instead of protons makes it possible to neutralize the most acidic Brønsted and Lewis sites of the zeolite, which reduces the secondary cracking of the molecules of gasoline middle distillates during the hydrocracking reactions. This result makes it possible to obtain a gain in selectivity of middle distillates. If the quantity of alkaline cations and preferably of Na^+ cations remaining in the structure of the modified zeolite is too large, the number of Brønsted acid sites decreases too greatly, which produces a loss of activity of the catalyst.

The process for modification of the zeolite next comprises at least one heat treatment stage d'). This heat treatment makes possible both the decomposition of the molecular compound that contains at least one silicon atom deposited on the zeolite at the end of stage b'), and the transformation of the NH_4^+ cations, partially exchanged at the end of stage c'), into protons. The heat treatment according to the invention is carried out at a temperature that is preferably between 200 and 700°C, more preferably between 300 and 500°C. Said heat treatment stage is advantageously implemented in air, under oxygen, under hydrogen, under nitrogen or under argon, or under a mixture of nitrogen and argon. The duration of this treatment is advantageously between 1 and 5 hours. At

the end of said heat treatment stage d'), a layer of amorphous silica is deposited on the surface of each of the crystals of the zeolite, and the protons of the zeolite are partially regenerated.

The Amorphous or Poorly Crystallized Oxide-Type Porous Mineral Matrix

The substrate of the hydroisomerization catalyst that is used in stage c) of the process according to the invention advantageously contains a porous mineral matrix, preferably amorphous, which advantageously consists of at least one refractory oxide. Said matrix is advantageously selected from the group that is formed by alumina, silica, clays, titanium oxide, boron oxide, and zirconia. The matrix can consist of a mixture of at least two of the oxides cited above, and preferably silica-alumina. It is also possible to select the aluminates. It is preferred to use matrices that contain alumina in all of these forms that are known to one skilled in the art, for example gamma-alumina.

It is also advantageously possible to use mixtures of alumina and silica, and mixtures of alumina and silica-alumina.

Preparation of the Catalyst

The modified zeolite can be, without this being limiting, for example, in the form of powder, ground powder, suspension, and a suspension that has undergone a deagglomeration treatment. Thus, for example, the modified zeolite can advantageously be put into a suspension that may or may not be slightly acidic at a concentration that is adjusted to the final zeolite content that is targeted in the substrate. This suspension, commonly called a slip, is then advantageously mixed with the precursors of the matrix.

According to a preferred preparation method, the modified zeolite can advantageously be introduced during the shaping of the substrate with the elements that constitute the matrix. For example, according to this preferred method of this invention, the modified zeolite according to the invention is added to a moist alumina gel during the stage for shaping the substrate.

One of the preferred methods of the shaping of the substrate in this invention consists in kneading at least one modified zeolite with a moist alumina gel for several

tens of minutes, and then in passing the thus obtained paste through a die for forming extrudates with a diameter of between 0.4 and 4 mm.

According to another preferred preparation method, the modified zeolite can be introduced during the synthesis of the matrix. For example, according to this preferred method of this invention, the modified zeolite is added during the synthesis of the silico-aluminum matrix; the zeolite can be added to a mixture that consists of an alumina compound in an acidic medium with a completely soluble silica compound.

The substrate can be shaped by any technique that is known to one skilled in the art. The shaping can be carried out, for example, by extrusion, by pelletizing, by the drop (oil-drop) coagulation method, by turntable granulation or by any other method that is well known to one skilled in the art.

At least one calcination cycle can be carried out after any of the stages of the preparation. The calcination treatment is usually carried out in air at a temperature of at least 150°C, preferably at least 300°C, and in a more preferred manner between about 350 and 1,000°C.

The elements of group VIII and/or the elements of group VIB, optionally at least one doping element that is selected from among boron, silicon, and phosphorus, and optionally the elements of groups IVB and IB in the case of a catalyst with a reduced nickel base, optionally can be introduced, completely or partially, at any stage of the preparation, during the synthesis of the matrix, preferably during the shaping of the substrate, or in a very preferred manner after the shaping of the substrate by any method that is known to one skilled in the art. They can be introduced after the shaping of the substrate and after or before the drying and the calcination of the substrate.

According to a preferred method of this invention, all or part of the elements of group VIII and/or the elements of group VIB, optionally at least one doping element that is selected from among boron, silicon and phosphorus, and optionally the elements of groups IVB and IB in the case of a catalyst with a reduced nickel base can be introduced during the shaping of the substrate, for example during the stage for kneading the modified zeolite with a moist alumina gel.

According to another preferred method of this invention, all or part of the elements of the group VIII, optionally at least one doping element that is selected from

among boron, silicon, and phosphorus, and optionally the elements of groups IVB and IB in the case of a catalyst with a reduced nickel base can be introduced by one or more operations for impregnation of the substrate that is shaped and calcined by a solution that contains the precursors of these elements. In a preferred way, the substrate is impregnated by an aqueous solution. The impregnation of the substrate is preferably carried out by the so-called "dry" impregnation method that is well known to one skilled in the art.

The following doping elements: boron and/or silicon and/or phosphorus can be introduced into the catalyst at any level of the preparation and according to any technique that is known to one skilled in the art.

In the case where the catalyst of this invention contains at least one metal of group VIII, the metals of group VIII are preferably introduced by one or more operations for impregnation of the substrate that is shaped and calcined, and after those of group VIB or at the same time as the latter, in the case where said catalyst contains at least one metal of group VIII combined with at least one metal of group VIB.

For example, among the sources of molybdenum and tungsten, it is possible to use oxides and hydroxides, the molybdic and tungstic acids and their salts, in particular ammonium salts such as ammonium molybdate, ammonium heptamolybdate, ammonium tungstate, phosphomolybdic acid, phosphotungstic acid, and salts thereof, silicomolybdic acid, silicotungstic acid, and salts thereof. The oxides and salts of ammonium such as the ammonium molybdate, ammonium heptamolybdate, and ammonium tungstate are preferably used.

The sources of non-noble elements of group VIII that can be used are well known to one skilled in the art. For example, for the non-noble metals, nitrates, sulfates, hydroxides, phosphates, halides such as, for example, chlorides, bromides and fluorides, and carboxylates, such as, for example, acetates and carbonates, will be used.

The sources of noble elements of group VIII that can advantageously be used are well known to one skilled in the art. For the noble metals, halides, for example, chlorides, nitrates, acids such as hexachloroplatinic acid, hydroxides, and oxychlorides such as ammoniacal ruthenium oxychloride, are used. It is also possible advantageously

to use the cationic complexes such as the ammonium salts when it is desired to deposit the metal on the Y-type zeolite by cationic exchange.

The noble metals of group VIII of the catalyst of this invention can advantageously be present completely or partially in metallic and/or oxide form.

The promoter element(s) selected from the group that is formed by silicon, boron and phosphorus can advantageously be introduced by one or more impregnation operations with excess solution on the calcined precursor.

The boron source can advantageously be boric acid, preferably orthoboric acid H_3BO_3 , ammonium biborate or pentaborate, boron oxide, and boric esters. Boron can be introduced, for example, in the form of a mixture of boric acid, hydrogen peroxide, and a basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the family of pyridine, and quinolines, and the compounds of the pyrrole family. Boron can be introduced by, for example, a boric acid solution in a water/alcohol mixture. The preferred phosphorus source is the orthophosphoric acid H_3PO_4 , but its salts and esters, such as the ammonium phosphates, are also suitable. Phosphorus can be introduced, for example, in the form of a mixture of phosphoric acid and a basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family, and quinolines and compounds of the pyrrole family.

Numerous silicon sources can advantageously be used. Thus, it is possible to use ethyl orthosilicate $\text{Si}(\text{OEt})_4$, siloxanes, polysiloxanes, silicones, silicone emulsions, halide silicates such as the ammonium fluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ or sodium fluorosilicate Na_2SiF_6 . The silicomolybdic acid and its salts, and the silicotungstic acid and its salts can also advantageously be used. Silicon can advantageously be added by, for example, impregnation of ethyl silicate in solution in a water/alcohol mixture. The silicon can be added by, for example, impregnation of a silicone-type silicon compound or the silicic acid suspended in water.

The element sources of group IB that can be used are well known to one skilled in the art. For example, among the copper sources, it is possible to use copper nitrate $\text{Cu}(\text{NO}_3)_2$.

The element sources of group IVB that can be used are well known to one skilled in the art. For example, among tin sources, it is possible to use tin chloride SnCl_2 .

The catalysts that are used in the process according to the invention advantageously have the shapes of spheres or extrudates. It is advantageous, however, that the catalyst comes in the form of extrudates with a diameter of between 0.5 and 5 mm and more particularly between 0.7 and 2.5 mm. The shapes are cylindrical (which can be hollow or not), braided cylindrical, multilobe (2, 3, 4 or 5 lobes, for example), rings. The cylindrical shape is used in a preferred manner, but any other shape can be used. The catalysts according to the invention optionally can be manufactured and used in the form of crushed powder, tablets, rings, balls, and wheels.

According to the invention, the metals of group VIB and/or of group VIII of said catalyst are present in sulfur form, the sulfurization treatment being described below.

In the case where the hydroisomerization catalyst contains at least one noble metal, the noble metal that is contained in said hydroisomerization catalyst is advantageously to be reduced. One of the preferred methods for conducting the reduction of metal is the treatment under hydrogen at a temperature of between 150°C and 650°C and a total pressure of between 1 and 250 bar. For example, a reduction consists of a stage at 150°C of two hours and then an increase in temperature up to 450°C at the rate of $1^\circ\text{C}/\text{minute}$, and then a stage of two hours at 450°C ; during this entire reduction stage, the flow rate of hydrogen is $1,000 \text{ normal m}^3 \text{ of hydrogen/m}^3 \text{ of catalyst}$, and the total pressure is kept constant at 1 bar. The entire ex-situ reduction method can advantageously be taken into consideration.

According to stage c) for hydroisomerization of the process according to the invention, at least one portion of the hydrocarbon base that is obtained from stage b) is brought into contact, in the presence of hydrogen, with said hydroisomerization catalyst, at temperatures and operating pressures that advantageously make it possible to carry out hydroisomerization of the non-converting feedstock. This means that the hydroisomerization is performed with a conversion of the $150^\circ\text{C}+$ fraction into the $150^\circ\text{C}-$ fraction that is less than 20% by weight, in a preferred manner less than 10% by weight, and in a very preferred manner less than 5% by weight.

Thus, according to the invention, the hydroisomerization stage c) of the process according to the invention is performed at a temperature of between 150 and 500°C, preferably between 150°C and 450°C, and in a very preferred manner between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, preferably between 2 MPa and 10 MPa, and in a very preferred manner between 1 MPa and 9 MPa, at an hourly volumetric flow rate that is advantageously between 0.1 h⁻¹ and 10 h⁻¹, preferably between 0.2 and 7 h⁻¹, and in a very preferred manner between 0.5 and 5 h⁻¹, at a flow rate of hydrogen such that the hydrogen/hydrocarbon volumetric ratio is advantageously between 70 and 1,000 Nm³/m³ of feedstock, between 100 and 1,000 normal m³ of hydrogen per m³ of feedstock, and in a preferred manner between 150 and 1,000 normal m³ of hydrogen per m³ of feedstock.

In a preferred manner, the optional hydroisomerization stage operates in co-current.

Techniques of Characterization

The quantity of alkaline cation that belongs to group IA or IIA of the periodic table, and preferably the quantity of alkaline cation Na⁺ remaining in the modified zeolite after the modification treatment described above, is measured by atomic adsorption according to a method that is known to one skilled in the art.

The Lewis and Brønsted acidity of zeolites is measured by adsorption of pyridine followed by infra-red spectroscopy (FTIR). The integration of the characteristic bands of the pyridine coordinated at 1,455 cm⁻¹ and protonated pyridine at 1,545 cm⁻¹ makes it possible to compare the relative acidity of the catalysts of the Lewis and Brønsted types, respectively. Before adsorption of the pyridine, the zeolite is pretreated under secondary vacuum at 450°C for 10 hours with an intermediate stage at 150°C for 1 hour. The pyridine is next adsorbed at 150°C and then desorbed under secondary vacuum at this same temperature before the spectra are taken.

The products, gas oil- and kerosene-based, obtained according to the process of the invention, are endowed with excellent characteristics.

The gas oil base that is obtained is of excellent quality:

- Its sulfur content is less than 10 ppm by weight.

- Its total aromatic compound content is less than 5% by weight, and the polyaromatic compound content is less than 2% by weight.
- The cetane number is excellent, higher than 55.
- The density is less than 840 kg/m^3 , and most often less than 820 kg/m^3 .
- Its kinematic viscosity at 40°C is 2 to $8 \text{ mm}^2/\text{s}$.
- Its cold strength properties are compatible with the standards in force, with a filterability boundary temperature at -15°C and a cloud point that is less than -5°C .

The kerosene that is obtained has the following characteristics:

- A density of between 775 and 840 kg/m^3
- A viscosity at -20°C less than $8 \text{ mm}^2/\text{s}$
- A crystal disappearance point of below -47°C
- A flash point of more than 38°C
- A smoke point of more than 25 mm

Examples

Stage a): Hydrotreatment

170 g/h of pre-refined canola oil with a density of 920 kg/m^3 that has a sulfur content of less than 10 ppm by weight, with a cetane number of 35, and whose composition is presented in detail below, is introduced into a reactor that is temperature-regulated in such a way as to ensure an isothermal operation and that has a fixed bed charged with 190 ml of hydrotreatment catalyst based on nickel and molybdenum, having a nickel oxide content that is equal to 3% by weight, and a molybdenum oxide content that is equal to 16% by weight and a P_2O_5 content that is equal to 6%, whereby the catalyst is sulfurized in advance:

Fatty Acid Glycerides	Nature of the Fatty Chain	% by Mass
Palmitic	C16:0	4
Palmitoleic	C16:1	< 0.5
Stearic	C18:0	2
Oleic	C18:1	61
Linoleic	C18:2	20
Linoleic	C18:3	9
Arachidic	C20:0	< 0.5
Gadoleic	C20:1	1
Behenic	C22:0	< 0.5
Erucic	C22:1	< 1

700 Nm³ of hydrogen/m³ of feedstock is introduced into the reactor that is kept at a temperature of 300°C and at a pressure of 5 MPa.

Stage b): Separation of the Effluent that is Obtained from Stage a).

The entire hydrotreated effluent that is obtained from stage a) is separated so as to recover the hydrogen-rich gases and a hydrocarbon base.

Stage c): Hydroisomerization of the Hydrotreated Effluent that is Obtained from Stage b) on a Catalyst According to the Invention

Preparation of the Modified Zeolite Used in the Catalyst According to the Invention.

100 g of dealuminified HY zeolites, with an Si/Al framework ratio that is equal to 11.5 and measured by NMR of silicon and aluminum, is exchanged by an NaNO₃ solution to obtain the NaY cationic form of the Y zeolite. The exchange is carried out in a flask that contains 1 L of NaNO₃ solution at 80°C for 2 hours, and then the suspension is filtered, and the zeolite is dried at 120°C for one night. The NaY zeolite that is obtained is poured into a three-neck flask that contains 1 L of anhydrous toluene and is equipped with a coolant. After an increase in temperature to 60°C, the quantity of

molecular compound tetraethylorthosilicate TEOS corresponding to 1% by weight of silica is slowly introduced into the zeolite suspension by using a syringe pump. After stirring for 1 hour, the suspension is filtered, and the zeolite is dried at 120°C for one night. The modified zeolite is then exchanged 3 times by a 1N solution of NH_4NO_3 to obtain the partially exchanged NH_4^+ form, whereby the exchange is carried out at a temperature of 80°C. The decomposition of the TEOS and the transformation of NH_4^+ cations into protons is done under H_2O -saturated N_2 at 350°C for 2 hours, and then a heat treatment under pure N_2 is done at 450°C for 2 hours. The characterizations of the zeolites that are measured by atomic adsorption spectroscopy and adsorption of pyridine followed by infrared are provided in Table 1.

Table 1: Characterization of the Samples.

	Anomalous Unmodified HY	Modified Y Exchanged 3 Times (According to the Invention)
Na / Al	0.001	0.05
Quantity of Na^+ remaining relative to the quantity of NH_4^+ that was initially present (%)	0.1	5.0
Brønsted acid sites (i.a., 1545 cm^{-1} band) after desorption of pyridine at 150°C	5.5	5.0
Lewis acid sites (i.a., 1455 cm^{-1} band) after desorption of pyridine at 150°C	3.7	1.5

An unmodified HY zeolite that is not in accordance with the invention is called a dealuminified HY zeolite that is exchanged by an NH_4NO_3 solution to obtain the cationic form of the Y zeolite but that has not been modified according to the modification process that is described according to the invention.

The analytical results show that the quantity of Brønsted acid sites slightly decreases and that the quantity of Lewis acid sites greatly decreases on the modified zeolites. This acidity variation varies in inverse proportion to the quantity of sodium present in the samples.

Preparation of the Catalysts

The catalyst substrates according to the invention containing zeolites that may or may not be modified are produced by using 19.5 g of zeolite mixed with 80.5 g of a matrix that consists of ultrafine tabular boehmite or alumina gel marketed under the name SB3 by the Condéa Chemie GmbH Company. This powder mixture is then mixed with an aqueous solution that contains nitric acid at 66% by weight (7% by weight of acid per gram of dry gel), and then kneaded for 15 minutes. The kneaded paste is then extruded through a die with a 1.2 mm diameter. The extrudates are next calcined at 500°C for 2 hours in air.

The thus prepared substrate extrudates are impregnated in the dry state by a solution of a mixture of ammonium heptamolybdate and nickel nitrate and calcined in air at 550°C in situ in the reactor. The contents by weight of oxides of the catalysts that are obtained are indicated in Table 2.

Table 2: Characteristics of the Catalysts.

Catalyst-Based Zeolite	Unmodified HY	Modified Y Exchanged 3 Times According to the Invention
MoO ₃ (% by weight)	12.1	12.4
NiO (% by weight)	3.2	3.1
Overall SiO ₂ (% by weight)	14.7	14.1
Make-up to 100% (for the most part composed of Al ₂ O ₃ (% by weight)	70.0	70.4

The hydrotreated hydrocarbon effluent that is obtained at the end of stage b) is hydroisomerized with hydrogen that is lost in a hydroisomerization reactor under the operating conditions below:

- VVH (volume of feedstock/volume of catalyst/hour) = 1 h⁻¹
- Total working pressure: 5 MPa
- Temperature: 300°C
- Hydrogen/Feedstock ratio: 700 normal liters/liter

The reaction temperature is set so as to achieve a gross conversion (denoted CB) that is equal to 70% by weight.

50 ppm by weight of dimethyl disulfide is added to the feedstock so as to simulate the partial pressures of H₂S and to keep the catalyst in sulfide form. The thus prepared feedstock is injected into the hydroisomerization test unit that comprises a fixed-bed reactor with upward circulation of the feedstock (“up-flow”) into which 100 ml of catalyst is introduced. The catalyst is sulfurized by a direct distillation gas oil/DMDS and aniline mixture up to 320°C. Note that any in-situ or ex-situ sulfurization method is

suitable. Once the sulfurization is carried out, the feedstock can be transformed. The operating conditions of the test unit are indicated above.

The jet fuel yield (kerosene, 150-250°C fraction, Kero yield hereinafter) is equal to the percentage by weight of compounds that have a boiling point of between 150 and 250°C in the effluents. The gas oil yield (250°C+ fraction) is equal to the percentage by weight of compounds that have a boiling point that is greater than 250°C in the effluents.

The temperature of 300°C is adjusted so as to have a conversion of the 150°C+ fraction into the 150°C- fraction that is less than 5% by weight during the hydroisomerization in the case where the hydroisomerization catalyst that is used in stage c) of the process according to the invention contains the modified zeolite according to the invention. In Table 3, we recorded the temperature of the yields in kerosene and gas oil for the catalysts described in the examples above.

Table 3: Catalytic Activities of the Hydroisomerization Catalysts.

	150°C- Yield	Kerosene Yield (% by Weight)	Gas Oil Yield (% by Weight)
Unmodified HY	13	30	57
Modified Y, Exchanged 3 Times (According to the Invention)	5	33	62

At a temperature of 300°C, the process that implements a catalyst containing an unmodified zeolite entrains the production of a 150°C- light fraction with a yield of 13% and therefore the production of middle distillates with a yield that is lower relative to the implementation of a catalyst that contains a modified zeolite according to the invention. The process according to the invention therefore demonstrates that the catalyst that contains a modified zeolite according to the invention and that is used in said process according to the invention is more active than the anomalous catalysts for obtaining a level of conversion of the 150°C+ fraction that is less than 5% by weight, while making it

possible to obtain higher middle distillate yields, and therefore a better selectivity of middle distillates, relative to a hydroisomerization process that implements an anomalous catalyst that contains an unmodified zeolite or a zeolite that is modified in a manner that is not in accordance with the invention.

CLAIMS

1. Process for treatment of feedstocks obtained from a renewable source and comprising the following stages:

a) Hydrotreatment of said feedstock in the presence of a fixed-bed catalyst that comprises a hydro-dehydrogenating function comprising at least one metal of group VIII and/or group VIB, taken by itself or in a mixture, and a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals, whereby said hydrotreatment stage operates at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 h⁻¹ and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³ of hydrogen/m³ of feedstock,

b) Separation, starting from the effluent that is obtained from stage a), of hydrogen, gases, and at least one hydrocarbon base,

c) Hydroisomerization of at least a portion of said hydrocarbon base that is obtained from stage b) in the presence of a fixed-bed hydroisomerization catalyst, whereby said catalyst comprises at least one hydro-dehydrogenating metal that is selected from the group that is formed by the metals of group VIB and group VIII of the periodic table and a substrate that comprises a zeolite that comprises at least one series of channels whose opening is defined by a ring with 8 oxygen atoms, modified by a') at least one stage for introducing at least one alkaline cation that belongs to group IA or IIA of the periodic table, b') a stage for treatment of said zeolite in the presence of at least one molecular compound that contains at least one silicon atom, c') at least one stage for partial exchange of said alkaline cations by NH₄⁺ cations, and d') at least one heat treatment stage, whereby said hydroisomerization stage is carried out at a temperature of between 150 and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly volumetric flow rate of between 0.1 and 10 h⁻¹, and in the presence of a total quantity of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1,000 Nm³/m³ of feedstock,

- d) Separation, starting from the effluent that is obtained from stage c), of hydrogen, gases, and at least one gas oil base and one kerosene base.
2. Process according to Claim 1, in which the element of group VIII is selected from among platinum and palladium, taken by themselves or in a mixture.
3. Process according to Claim 2, in which said catalyst comprises, in % by weight relative to the total mass of the catalyst, a content of noble metal of between 0.01 and 10% by weight.
4. Process according to Claim 1, in which the catalyst comprises at least one metal of group VIB in combination with at least one non-noble metal of group VIII, whereby the metal content of group VIB encompasses, in oxide equivalent, between 5 and 40% by weight relative to the total mass of said catalyst, and the content of non-noble metal of group VIII encompasses, in oxide equivalent, between 0.5 and 10% by weight relative to the total mass of said catalyst.
5. Process according to Claim 4, in which the non-noble element of group VIII is selected from among iron, cobalt and nickel, taken by themselves or in a mixture.
6. Process according to one of Claims 4 or 5, in which the element of group VIB is selected from among tungsten and molybdenum.
7. Process according to one of Claims 1 to 6, in which the zeolite that is contained in the substrate of the catalyst that is used in stage c) of the process according to the invention is selected from among the zeolites Y, ZSM-48, ZBM-30, IZM-1 and COK-7, taken by themselves or in a mixture.
8. Process according to Claim 7, in which the initially used zeolite is the Y zeolite.
9. Process according to one of Claims 1 to 8, in which said alkaline cation that belongs to the groups IA and IIA introduced in stage a) is selected from among the cations Na^+ , Li^+ , K^+ , Rb^+ , Cs^+ , Ba^{2+} and Ca^{2+} , and, preferably, said cation is the Na^+ cation.
10. Process according to one of Claims 1 to 9, in which the molecular compound that contains at least one silicon atom that is used in the treatment stage b) is selected from among the compounds of formula Si-R_4 and $\text{Si}_2\text{-R}_6$ where R is selected from

among hydrogen, an alkyl, aryl or acyl group, an alkoxy group (O-R'), a hydroxyl group (-OH), or a halogen.

11. Process according to one of Claims 1 to 10, in which the content of alkaline cations remaining in the modified zeolite at the end of stage c) is such that the alkaline cation/aluminum molar ratio is between 0.2:1 and 0.01:1.

12. Process according to Claim 11, in which the content of alkaline cations remaining in the modified zeolite at the end of stage c) is such that the alkaline cation/aluminum molar ratio is between 0.2:1 and 0.015:1.

13. Process according to Claim 11, in which the content of alkaline cations remaining in the modified zeolite at the end of stage c) is such that the alkaline cation/aluminum molar ratio is between 0.15:1 and 0.02:1.

14. Process according to one of Claims 1 to 13, in which the feedstocks that are obtained from renewable sources are selected from among the oils and fats of plant or animal origin, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters and said vegetable oils that can be raw or refined, totally or partially, and obtained from the following plants: canola, sunflower, soybean, palm, palm-kernel, olive, coconut, jatropha, and the animal fats being selected from among lard or fats composed of waste from the food industry or obtained from catering industries.