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(54) **OPTIMIZED PROCESS FOR UPGRADING
BIO-OILS OF AROMATIC BASES**

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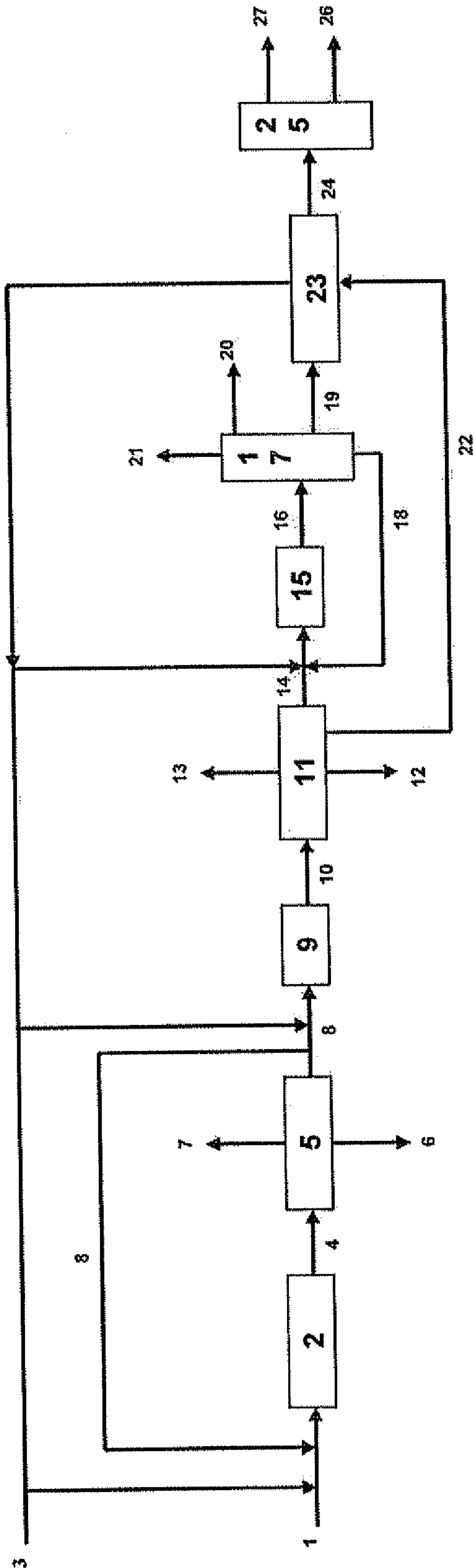
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(57) **ABSTRACT**

A process for preparing aromatic compounds from a liquid biofuel feedstock by introducing the feedstock into a hydrotreating stage in the presence of hydrogen and a hydrotreating catalyst that contains a transition metal of a group 3 to 12 element and an activated carbon, silicon carbide, silica, transition alumina, alumina-silica, zirconium oxide, cerium oxide, titanium oxide, or an aluminate of a transition metal substrate, to obtain a liquid effluent that contains an aqueous phase and an organic phase, a stage for hydrotreatment of the organic phase, a hydrocracking stage, recycling a fraction that boils higher than 160° C. in said hydrocracking stage, a separation into a fraction containing naphtha and a fraction that boils higher than 160° C., a stage for catalytic reforming of the fraction containing naphtha to obtain hydrogen and a reformat that contains aromatic compounds and a stage for separation of the aromatic compounds of the reformat.

FIG. 1



OPTIMIZED PROCESS FOR UPGRADING BIO-OILS OF AROMATIC BASES

FIELD OF THE INVENTION

[0001] This invention relates to a process for the production of aromatic compounds starting from liquids obtained from biomass and in particular starting from liquefied biomass obtained from the pyrolysis of biomass, also called bio-oil. In a more specific manner, the invention relates to a process for conversion of bio-oil into BTX-type aromatic compounds comprising a hydrotreating stage, followed by a hydrocracking stage in a fixed bed of rigorous conditions suitable for maximizing the production of light aromatic precursors and a catalytic reforming stage.

STATE OF THE ART

[0002] The aromatic compounds, in particular the C6-C8 aromatic compounds, i.e., benzene, toluene and xylenes/ethylbenzene (BTX), are major intermediate compounds in petrochemistry for the synthesis of resins, plasticizers and polyester fibers.

[0003] The primary BTX production source is the catalytic reforming (or aromatizing according to English terminology) that is used by refiners for improving the octane number of the gasoline by manufacturing aromatic compounds. Starting from naphtha, this process produces a fraction that is rich in aromatic hydrocarbons, called reformate, from which it is possible to extract, separate and transform the aromatic compounds.

[0004] Today, the production of aromatic compounds is based essentially on a petroleum origin. The current international context is first marked by a desire to reduce dependency as regards raw materials of fossil origin and then owing to the significance of the problems linked to global warming and greenhouse gas emissions. In this context, the search for new feedstocks obtained from non-fossil sources constitutes stakes of growing importance. Among these feedstocks, it is possible to cite, for example, biomass.

[0005] Taking into account abundant and renewable biomass reserves, an attractive alternative for the production of intermediate products in petrochemistry is the use of liquids obtained from biomass, in general also called bio-oil or else bio-crude.

[0006] The liquid products that are obtained by thermochemical liquefaction of cellulosic biomass are called bio-oils. The process for thermochemical liquefaction of biomass can be performed, for example, with or without the presence of catalyst, in the presence of a cover gas or a gas that contains hydrogen and water. The thermochemical processes in general convert the biomass into liquid, gaseous, and solid products. Among these processes, those called rapid pyrolysis processes tend to maximize the liquid yield. During rapid pyrolysis, the temperature of the biomass, optionally divided, is quickly raised to values that are higher than approximately 300° C. and preferably between 450 and 600° C. and in a preferred manner between 450 and 550° C., and the liquid products are condensed in the form of bio-oil. Ringer et al. (*Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis*, M. Ringer, V. Putsche, and J. Scallan, NREL Technical Report NREL/TP-510-37779, November 2006) studied the different technologies implemented for the rapid pyrolysis of biomass on a large scale. They comprise boiling fluidized beds, circulating fluidized

beds, ablative pyrolysis reactors, vacuum pyrolysis reactors, and rotating cone pyrolysis reactors.

[0007] The bio-oils and in particular the bio-oils obtained from the rapid pyrolysis of biomass are complex mixtures of greatly oxygenated polar hydrocarbon-containing products obtained from the breakage of biopolymers and having physical and chemical properties limiting their direct use.

[0008] The bio-oils of pyrolysis have undesirable properties such as: (1) The corrosiveness due to their high content of water and organic acids; (2) A low specific calorific value because of the high content of oxygen, typically on the order of 40% by weight; (3) Chemical instability, in storage as well as under elevated heat conditions, due to the abundance of reactive oxygenated functional groups such as the carbonyl group, which can bring about polymerization during storage and consequently a separation of phases; (4) A viscosity and a tendency toward the separation of relatively high phases under high shearing conditions, in an injector, for example; (5) Solid coal particles obtained from pyrolysis, which will always be present in non-filtered bio-oils in small amounts such that the bio-oil/coal particles ratio is higher than 10:1 and preferably higher than 50:1. However, said particles can cause the clogging of stationary internal combustion engines or can poison post-treatment catalysts.

[0009] All of these aspects are combined to make handling, shipping, storage and use of the bio-oils difficult and costly, thus making their integration into the systems and the current technologies for production of heat and energy very problematic.

[0010] During the last twenty years, the approach consisting in carrying out direct hydrotreatment of bio-oil for the purpose of converting it into hydrocarbons or stable oxygenated liquids has been the object of intensive studies. Elliott published a detailed study of these numerous historical developments, including the work done with model compounds known for being present in the bio-oils (*Historical Developments in Hydroprocessing BioOils*, D. C. Elliott, Energy & Fuels 2007, 21, 1792-1815).

[0011] One of the major obstacles to the direct catalytic hydrotreatment of bio-oils resides in their tendency to polymerize when they are subjected to higher temperatures than approximately 100° C., which gives rise to the formation of solids at higher temperatures than approximately 140° C., with consequences such as the clogging of feedstock lines, furnaces and reactors as well as the rapid deactivation of the catalyst, and even the clogging of the inlet of the reactor.

[0012] Nevertheless, an effective hydrotreatment process remains to be found. The difficulties encountered find their origin in the rapid thermal polymerization of bio-oil, which leads to the clogging of lines and reaction equipment as well as to rapid deactivation of the catalyst. In other words, with temperatures that are typically required for the hydrotreatment of bio-oils, the polymerization reactions are essentially faster than the hydrotreatment reactions, which ultimately bring about the formation of solid in the equipment under reaction conditions. Furthermore, the consumption of hydrogen of this type of hydrotreatment remains very high: from 4 to 6% relative to the initial dry biomass.

[0013] There is therefore a need for an improved process for hydrotreatment of bio-oils that minimizes the formation of solids, the deactivation of catalyst, and the consumption of hydrogen, and that maximizes the yield of deoxygenated oil that is produced.

[0014] The purpose of this invention is to produce BTX-type aromatic compounds from a liquid feedstock that comprises at least one bio-oil by using a process that comprises a hydrotreating stage, followed by a hydrocracking and catalytic reforming stage.

SUMMARY OF THE INVENTION

[0015] This invention relates to a process for the production of aromatic compounds, in particular of the BTX type, starting from a liquid feedstock that comprises at least one bio-oil, whereby said feedstock is introduced into at least the following stages:

[0016] A first hydrotreating stage in the presence of hydrogen and a hydrotreating catalyst comprising at least one transition metal that is selected from among the elements of groups 3 to 12 of the periodic table and at least one substrate that is selected from among the activated carbons, silicon carbides, silicas, transition aluminas, alumina-silicas, zirconium oxide, cerium oxide, titanium oxide and the transition metal aluminates, taken by themselves or in a mixture, for obtaining at least one liquid effluent that comprises at least one aqueous phase and at least one organic phase,

[0017] A second stage for hydrotreatment of at least one portion of the organic phase of the effluent that is obtained from the first hydrotreating stage in the presence of hydrogen in at least one reactor that contains a hydrotreatment catalyst, operating at a temperature of between 250 and 400° C., at a pressure of between 2 MPa and 25 MPa, at an hourly volumetric flow rate of between 0.1 h⁻¹ and 20 h⁻¹, and with a total amount of hydrogen mixed with the feedstock such that the hydrogen/hydrocarbon volumetric ratio is between 100 and 3,000 Nm³/m³,

[0018] A third stage for hydrocracking at least one portion of the effluent that is obtained from the second hydrotreatment stage, in the presence of hydrogen, in at least one reactor that contains a hydrocracking catalyst, operating at a temperature of between 250 and 480° C., under a pressure of between 2 and 25 MPa, at a volumetric flow rate of between 0.1 and 20 h⁻¹, and with an amount of hydrogen that is introduced such that the hydrogen to hydrocarbon volumetric ratio is between 80 and 5,000 Nm³/m³, in which at least one portion of the fraction that boils at a temperature that is higher than 160° C., separated at the end of said third hydrocracking stage, is recycled in said third hydrocracking stage,

[0019] A separation of the effluent that is obtained at the end of the third hydrocracking stage into at least one fraction that contains naphtha and a fraction that boils at a temperature that is higher than 160° C.,

[0020] A fourth stage for catalytic reforming of the naphtha-containing fraction that is obtained from the separation operating in the presence of a catalytic reforming catalyst, under a pressure of between 0.1 and 4 MPa at a temperature of between 400 and 700° C., at a volumetric flow rate of between 0.1 and 10 h⁻¹, and with a hydrogen/hydrocarbon ratio of 0.1 to 10, making it possible to obtain hydrogen and a reformat that contains aromatic compounds,

[0021] A stage for separating aromatic compounds from the reformat that is obtained at the end of the catalytic reforming stage.

[0022] One advantage of this invention is to provide a process, starting from a liquid feedstock that comprises at least one bio-oil, comprising a hydrotreating stage followed by a hydrotreatment stage and then a hydrocracking stage that made it possible to obtain, after separation, a naphtha fraction that is particularly well suited by its naphtho-aromatic chemical nature and by its very small amount of impurities for the production of aromatic compounds by the catalytic reforming. Its unique structure imparts to it excellent reactivity relative to aromatization reactions.

[0023] In a first step, the hydrotreating stage makes it possible to obtain a liquid effluent that comprises at least one aqueous phase and at least one organic phase also containing large amounts of impurities: heteroelements of sulfur, nitrogen and oxygen as well as olefins and polyaromatic compounds. Before sending the light fraction (naphtha) of said organic phase into the catalytic reforming stage, it thus is necessary to carry out a hydrotreatment stage that makes possible the elimination of nitrogen-containing, oxygenated and sulfur-containing impurities, and then a stage of rigorous hydrocracking with recycling of the distilling fraction beyond 160° C. to maximize said naphtha. This hydrocracking stage thus makes it possible to obtain a significant naphtha fraction by cracking.

[0024] Likewise, the rigorous conditions of the hydrocracking stage make it possible to increase the naphtha fraction yield and therefore ultimately to increase the yield of aromatic compounds and hydrogen produced during the reforming.

DETAILED DESCRIPTION OF THE INVENTION

[0025] In accordance with the invention, the feedstock that comprises at least one bio-oil that is treated in the process according to the invention is a liquid feedstock. Throughout the rest of the text, liquid feedstock is defined as a feedstock that comprises less than 2% by weight, and preferably less than 1% by weight, relative to the bio-oil, of solid particles dispersed in a liquid. This corresponds to a bio-oil/solid particles ratio that is greater than 50:1 and preferably greater than 100:1. Said feedstock therefore is not a suspension.

[0026] A bio-oil is a complex mixture of oxygenated compounds, obtained from the breakage of biopolymers that are present in the original biomass. In the case of the lignocellulosic biomass, the structures that are obtained from these three primary components, cellulose, hemicellulose and lignin, are well represented by the components of the bio-oil.

[0027] In particular, a bio-oil is a highly-oxygenated polar hydrocarbon-containing product that in general comprises at least 10% by weight of oxygen, preferably 10 to 60% by weight of oxygen relative to the total mass of said bio-oil. In general, the oxygenated compounds are alcohols, aldehydes, esters, ethers, organic acids and aromatic oxygenated compounds. In the case where the bio-oil is obtained by rapid pyrolysis, a portion of the oxygen is present in the form of free water representing at least 5% by weight, preferably at least 10% by weight, and in a preferred manner at least 20% by weight of bio-oil. These properties make the bio-oil totally immiscible with the hydrocarbons, and even with the aromatic hydrocarbons that generally contain very little or no oxygen.

[0028] The bio-oils are advantageously obtained from the biomass and are preferably selected from among plants, grasses, trees, wood chips, seeds, fibers, seed husks, aquatic plants, hay, and other sources of lignocellulosic materials,

such as, for example, those coming from municipal waste, food-processing waste, lumber scrap, slaughterhouse waste, and agricultural and industrial waste (such as, for example, sugar cane debris, waste obtained from the cultivation of oil palm, sawdust or straw). The bio-oils can also come from paper paste and by-products of paper that may or may not be recycled, or by-products obtained from paper mills.

[0029] The bio-oils are advantageously obtained by thermochemical liquefaction of the biomass, preferably by pyrolysis, and, in a preferred manner, by rapid pyrolysis, or slow pyrolysis with or without a catalyst (in the presence of catalyst, mention is then made of catalytic pyrolysis). Pyrolysis is a thermal breakdown in the absence of oxygen, with thermal cracking of gas, liquid and solid feedstocks. A catalyst can advantageously be added for reinforcing the conversion during the so-called catalytic pyrolysis. The catalytic pyrolysis generally provides a bio-oil that has an oxygen content that is lower than that of the bio-oil obtained by thermal breakdown, but the bio-oil yield is generally lower. The selectivity between the gas, the liquid and the solid is in a ratio with the reaction temperature and the dwell time of the vapor. The processes for pyrolysis of the biomass, in particular rapid pyrolysis, are well described in the literature, such as, for example, in A. V. Bridgewater, H. Hofbauer, and S. van Loo, *Thermal Biomass Conversion*, CPL Press, 2009, 37-78.

[0030] Slow pyrolysis is advantageously carried out at a temperature of between 350 and 450° C. and preferably on the order of 400° C. and with a long dwell time of between several minutes and several hours, which promotes the production of a solid product that is also called a product of carbonization or wood carbon. In particular, slow pyrolysis generally makes possible the production of 35% by weight of gas, 30% by weight of liquid, and 35% by weight of carbonization product. The gasification processes operating at very high temperatures, preferably higher than 800° C., promote the production of gas, and in particular more than 85% by weight of gas. The intermediate pyrolysis is advantageously carried out at a temperature that is in general between 450 and 550° C. and with a short dwell time of the vapor, preferably between 10 and 20 seconds, which promotes the liquid yield. In particular, the intermediate pyrolysis in general makes possible the production of 30% by weight of gas, 50% by weight of liquid, and 20% by weight of carbonization product.

[0031] Rapid pyrolysis is advantageously carried out at a temperature of generally between 450 and 550° C. and with a very short dwell time of the vapor, preferably between 0.5 and 2 seconds, which maximizes the liquid yield: in particular, rapid pyrolysis in general makes possible the production of 10-20% by weight of gas, 60-75% by weight of liquid, and 10-20% by weight of carbonization product. The highest liquid yields are therefore obtained within the framework of the rapid pyrolysis processes of wood, with a liquid yield that can reach up to 75% by weight. A portion of the oxygen is present in the form of free water representing at least 5% by weight, preferably at least 10% by weight, and in a preferred manner at least 20% by weight of the bio-oil.

[0032] Preferably, the bio-oils that are used in the process according to this invention are obtained by rapid pyrolysis of the biomass.

[0033] The bio-oils can also advantageously be obtained by thermochemical liquefaction of the biomass such as, for example, by hydropyrolysis of the biomass. The liquid feedstock that is treated in the process according to the invention

preferably comprises a bio-oil content of between 10 and 100% by weight relative to the total mass of said feedstock.

[0034] The liquid feedstock that comprises at least one bio-oil that is used in the process according to the invention can also advantageously contain other liquid feedstocks that are obtained from the biomass, with said liquid feedstocks advantageously being selected from among vegetable oils, alga or algal oils, fish oils, fats of vegetable or animal origin, and alcohols obtained from the fermenting of sugars of the biomass, or mixtures of such feedstocks, which may or may not be pretreated. The vegetable oils or the oils that are derived from animal fats essentially comprise triglyceride-type chemical structures that one skilled in the art also knows under the name fatty acid triesters as well as free fatty acids, whose fat chains contain a carbon atom number of between 9 and 25.

[0035] Said vegetable oils can advantageously be crude or refined, totally or in part, and obtained from vegetables that are selected from among canola, sunflower, soybean, palm, olive, coconut, copra, castor oil, cotton, oils from peanuts, flax, and sea-cabbage, and all of the oils that are obtained from, for example, sunflower or canola by genetic modification or hybridization, with this list not being limiting. Said animal fats are advantageously selected from among the fats composed of residues from the food industry or obtained from the catering industry. Cooking oils, various animal oils such as fish oils, tallow and lard can also be used.

[0036] Said liquid feedstock comprising at least one bio-oil can also advantageously be treated in a mixture with at least one hydrocarbon-containing liquid feedstock that is derived from petroleum and/or coal. The petroleum-derived liquid hydrocarbon-containing feedstock can advantageously be selected from among the direct distillation vacuum distillates, the vacuum distillates originating from a conversion process, such as those obtained from processes of coking, hydroconversion in a fixed bed or hydrotreatment of heavy fractions in a boiling bed, the products obtained from fluid catalytic cracking units, such as, for example, the light diesel fuel of catalytic cracking (LCO) of different origins, the heavy diesel fuel of catalytic cracking (HCO) of different origins, and any fluid catalytic cracking distillate fraction that in general has a distillation interval of approximately 150° C. to approximately 370° C., the aromatic extracts and the paraffins obtained during the preparation of lubricating oils and oils that are deasphalted with solvent, by themselves or in a mixture. The coal-derived liquid hydrocarbon-containing feedstock can advantageously be selected from among the products that are obtained from the liquefaction of coal and the aromatic fractions originating from pyrolysis or gasification of coal and shale oils or products derived from shale oils, by themselves or in a mixture, pretreated or not.

[0037] To the extent that the hydrogen is produced on the inside during the hydrotreating stage of the liquid feedstock comprising at least one bio-oil, the consumption of hydrogen for the co-treatment in a mixture with the petroleum- and/or coal-derived hydrocarbon-containing feedstocks is reduced.

[0038] Preferably, said liquid feedstock comprising at least one bio-oil can advantageously be a mixture of one of any of the feedstocks cited above, with said feedstocks being able to be pretreated or not.

[0039] In a preferred variant, said treated liquid feedstock in the process according to the invention consists entirely of bio-oil.

[0040] Hydroreforming

[0041] In accordance with the invention, said liquid feedstock comprising at least one bio-oil, optionally at least one petroleum- and/or coal-derived liquid hydrocarbon-containing feedstock, optionally other liquid feedstocks obtained from biomass, optionally mixed with at least one portion of the organic phase of the effluent that is obtained from the hydroreforming stage that is recycled, is introduced into said first hydroreforming stage.

[0042] The reaction is designated here under the term of "hydroreforming" since it brings about a characteristic change in the distribution of molecular weight of the feedstock comprising at least one bio-oil. Preferably, the hydroreforming stage is a stage of the hydrotreatment/hydroconversion type in which the liquid feedstock comprises at least the bio-oil and preferably in which the bio-oil is partially deoxygenated and partially hydroconverted. Said hydroreforming stage is carried out with a partial production of hydrogen that is internal to the reaction.

[0043] In a preferred manner, said hydroreforming stage is a partial deoxygenation and partial hydroconversion stage. Partial deoxygenation and partial hydroconversion is defined as a reaction in which the oxygen content in the organic phase is reduced to a content of between 5 and 25% by weight, making it possible to obtain less than 20% by weight of a fraction boiling at a temperature that is higher than 600° C.

[0044] During said first hydroreforming stage, the bio-oil is transformed for the purpose of stabilizing the product, making it miscible with hydrocarbons, bringing about an easy water-phase separation in bio-oil, lowering its viscosity, lowering its corrosiveness, converting in particular the fractions of high molecule weight into smaller molecules and lowering its oxygen content.

[0045] The Product of the Hydroreforming Stage

[0046] In accordance with the invention, said first hydroreforming stage makes it possible to obtain at least one liquid effluent that comprises at least one aqueous phase and at least one organic phase.

[0047] A gaseous phase is also advantageously obtained, with said gaseous phase containing for the most part CO₂, CO, and C1-C4 light gases, such as, for example, methane. Said gaseous phase can advantageously be separated from said aqueous and organic phases in any separator that is known to one skilled in the art.

[0048] Said aqueous phase and said organic phase are advantageously separated by decanting.

[0049] The analysis of the liquid effluent does not show any sign of polymerization.

[0050] Said aqueous phase comprises water and can also comprise organic materials, primarily acetic acid and methanol (case of bio-oil of rapid pyrolysis), dissolved in said aqueous phase. The aqueous phase essentially contains water formed by hydrogenation-deoxygenation and water contained in the non-pretreated bio-oil that has not been converted and in general less than approximately 20% by weight of dissolved organic materials. For the pyrolysis bio-oils, the aqueous phase that is separated during the first reforming stage typically contains approximately 10% by weight of acetic acid and a smaller proportion of methanol. Preferably, the acetic acid and the methanol are recovered in the aqueous phase because they consist of upgradable by-products. Acetic acid can advantageously be recovered by different known means such as distillation or evaporation, crystallization in salt form, of an alkaline earth, for example, or by extraction

with solvent, by means of liquid ion exchangers, for example. Because of its low boiling point and the absence of formation of azeotropes with water, methanol is simply recovered by distillation. Preferably, acetic acid and methanol taken together comprise at least 80% by weight of organic components in the aqueous phase.

[0051] The organic phase contains partially deoxygenated bio-oil and hydrocarbons. Partially deoxygenated bio-oil is defined as a bio-oil that contains less than 25% by weight of oxygen and preferably less than 15% by weight of oxygen relative to the total mass of said organic phase. The organic phase therefore comprises less than 25% by weight of oxygen, preferably less than 15% by weight of oxygen, and in a preferred manner less than 10% by weight of oxygen relative to the total mass of said organic phase.

[0052] Thus, said organic phase is deoxygenated to a sufficient degree to make it miscible with hydrocarbon-containing feedstocks such as the ones used in a petroleum refinery at elevated concentrations. In general, said organic phase can be mixed freely with most of the hydrocarbon-containing products at concentrations that can reach at least 30% by weight. Furthermore, to the extent that the oxygen content is essentially reduced and the bio-oil is already partially converted, the hydrogen requirements during subsequent stages in the refinery are greatly minimized. In addition, said organic phase is stabilized in such a way as to be able to be treated subsequently in a refinery without running the risk of solids forming by polymerization or polycondensation.

[0053] The organic phase preferably contains less than 25% by weight of oxygen and preferably less than 15% by weight of oxygen and less than 5% by weight of water, preferably less than 2% by weight of water relative to the total mass of said organic phase. The consumption of hydrogen during said first hydroreforming stage is preferably less than approximately 2% by weight of bio-oil.

[0054] Preferably, the total acid number (TAN) is less than approximately 100 KOH/g of oil. The total acid number is expressed in terms of mg of KOH/g of oil. It is the amount of potassium hydroxide in milligrams that is necessary for neutralizing the acids in one gram of oil. There are standard methods for determining the acid number, such as the ASTM D 974 and DIN 51558 methods (for mineral oils, biodiesels), or methods that are specific to biodiesels using the European standards EN 14104 and ASTM D664, widely used on the world scale.

[0055] The higher calorific value (PCS) exceeds approximately 35 MJ/kg in the organic phase that is obtained from said first hydroreforming stage.

[0056] Typically, during the first hydroreforming stage, the organic phase yields relative to the dry biomass, i.e., comprising 0% moisture, introduced into the pyrolysis stage, are between 15 and 45% by weight, and preferably between 15 and 40% by weight. The aqueous phase yields relative to the dry biomass are between 10 and 50% by weight, and preferably between 10 and 40% by weight. The gaseous phase yields relative to the dry biomass are between 5 and 30% by weight. The conversion of the organic fraction of bio-oil into partially deoxygenated bio-oil represents at least 70% by weight.

[0057] According to one variant, at least one portion of the organic phase of the effluent that is obtained from the first hydroreforming stage is recycled in said first hydroreforming stage. Preferably, the recycling rate that is equal to the ratio of the mass flow rate of said organic phase to the mass flow rate

of the non-pretreated bio-oil is between 0.05 and 10, in a preferred manner between 0.05 and 5, and in a very preferred manner between 0.05 and 1.

[0058] The recycling rates that are used make it possible to have, overall, a feedstock that is stable enough thermally to be able to be introduced into the preheating furnace as well as into the hydroreforming reactor without running the risk of clogging, to facilitate the reactions of conversion and deoxygenation of the bio-oil on the catalyst, to improve the dissolution of gaseous hydrogen in the recycled organic phase that is obtained from the first hydroreforming stage, and to better manage the exothermicity generated by the reactions, while minimizing the recycling of all or part of the organic phase obtained from hydroreforming so as to minimize the investment costs as well as the operating costs.

[0059] The recycled organic phase in said first hydroreforming stage, and obtained from this stage, is also used to lower the volumetric mass of the partially deoxygenated bio-oil that is produced during this first stage, which facilitates the release of the partially deoxygenated bio-oil phase and the aqueous phase at the hydroreforming outlet. This separation that is easily done during the cooling of the reaction mixture is another advantage that the presence of the recycled organic phase obtains in the reaction mixture of the first hydroreforming stage.

[0060] Another advantage, the presence of the recycled organic phase in the reaction mixture, tends to expel water from said organic phase, the water content thus being as small as possible, which is favorable to the use of said organic phase as an industrial fuel or as a feedstock for subsequent treatment stages. Thus, said phase, said organic phase, obtained from the first hydroreforming stage contains less than 5% by weight of water, preferably less than 2%.

[0061] In accordance with the invention, the catalyst that is used in the first hydroreforming stage preferably comprises at least one transition metal that is selected from among the elements of groups 3 to 12 of the periodic table and at least one substrate selected from among the activated carbons, the silicon carbides, the silicas, the transition aluminas, the alumina-silicas, zirconium oxide, cerium oxide, titanium oxide, and the transition metal aluminates, taken by themselves or in a mixture. Preferably, the catalyst comprises a metal of group 10, by itself or in combination with at least one metal of groups 3 to 12, and in a preferred manner at least one metal of groups 5, 6, 8, 9, 10, and 11 of the periodic table. In a preferred manner, the catalyst comprises Ni, by itself or in combination with at least one metal that is selected from among Cr, Mo, W, Fe, Co and Cu.

[0062] The metal content of group 10 and preferably nickel, expressed in terms of percentage by weight of metal oxide of group 10, is advantageously between 1 and 20% by weight, preferably between 5 and 15% by weight relative to the total mass of said catalyst.

[0063] In the case where said metal of group 10 is used in combination with at least one metal of groups 3 to 12, the metal content of groups 3 to 12 is advantageously between 1 and 20% by weight relative to the total mass of said catalyst.

[0064] Preferably, the substrate is selected from among activated carbons, silicas, transition aluminas, silica-aluminas, and transition metal aluminates. These substrates can be taken by themselves or in a mixture.

[0065] Preferred catalysts are selected from among the catalysts comprising Ni, Cu, NiCr, NiMo or NiMn on activated carbon or on alumina or nickel aluminate.

[0066] Preferably, said catalyst is prepared according to the conventional methods such as co-mixing or impregnation followed by one or more heat treatments.

[0067] Said catalyst is advantageously used in the first hydroreforming stage in a reduced or sulfurized form.

[0068] Operating Conditions

[0069] Preferably, said first hydroreforming stage is carried out at a temperature of between 250 and 450° C., preferably between 250 and 400° C., and in a preferred manner between 270 and 360° C., and at an absolute pressure of between 3.4 and 27.6 MPa (500 and 4,000 psi), preferably between 3.4 and 20.7 MPa (500 and 3,000 psi), and in a preferred manner between 6.9 and 20.7 MPa (1,000 and 3,000 psi), and in a more preferred manner between 15 and 20.7 MPa, at an elevated hourly volumetric flow rate relative to bio-oil, preferably greater than 0.2 h⁻¹, in a preferred manner between 0.5 h⁻¹ and 5 h⁻¹, and in a more preferred manner between 1 h⁻¹ and 5 h⁻¹, and with an amount of hydrogen that is introduced such that the volumetric ratio of hydrogen to hydrocarbons is between 50 and 2,000 Nm³/m³ and preferably between 100 and 1,000 Nm³/m³.

[0070] Preferably, the liquid feedstock comprising at least bio-oil is not preheated, or only preheated to a temperature that is less than 80° C. before being introduced into the first hydroreforming stage. Actually, extended heating or storage at an elevated temperature can cause deterioration.

[0071] There are no limitations relative to the equipment designed to carry out the process. The latter can be conducted intermittently or continuously. Nevertheless, for large-scale industrial applications, it will be preferable to operate continuously.

[0072] The hydroreforming reaction can be carried out in any reactor that facilitates the effective dispersion of bio-oil in the reaction mixture. A simple perfectly stirred continuous reactor (CSTR) is suitable in intermittent mode. For continuous applications, downward co-current packed-bed reactors, moving-bed reactors, boiling-bed reactors or slurry reactors will be more suitable. While keeping the catalyst in the reactor, the technologies of moving-bed reactors and boiling-bed reactors offer the advantage of making possible the easy replacement of the catalyst during continuous operations, which imparts a greater flexibility to the operation of the unit, increases the operational factor and maintains activity based on near-constant time. These technologies also accept feedstocks that contain a few solids or that produce solids during reactions, which is not the case of the technology of a fixed-bed reactor, except in using reactors of switchable-guard reactors, for example. The technology of the slurry reactor, according to English terminology, offers the same advantages as the technologies of moving-bed reactors and boiling-bed reactors and the additional advantage of operating with a fresh catalyst, therefore with maximum activity, but the drawback of greatly complicating the recovery of the catalyst that exits from the reactor with the effluents. Other reactors that meet the principles indicated here are within the grasp of one skilled in the art who is versed in the technology of chemical reactors and are found within the framework of this invention.

[0073] Hydrogen Consumption

[0074] During the first hydroreforming stage, internal reforming of the bio-oil into carbon oxides and hydrogen oxides is done with a relatively high yield of hydrocarbons and a relatively low consumption of hydrogen. The hydrogen consumption is therefore moderated during the first hydroreforming stage, and the internal production of hydrogen by

hydroreforming makes it possible to perform the process with a very limited external consumption of hydrogen.

[0075] A portion of the hydrogen that is necessary to the reaction in the first hydroreforming stage is generated internally, a priori from water that is present in the bio-oil, by hydroreforming a portion of the bio-oil, in such a way that a significant portion of oxygen is released in the form of carbon dioxide, and the net hydrogen demand is to a large extent less than in the case of the direct hydrogenation-deoxygenation process. The other portion of hydrogen that is necessary to the reaction is of external origin. Typically, the hydrogen consumption during the first hydroreforming stage is less than approximately 2% by weight of the mass of bio-oil introduced into the reactor, and the corresponding emission of CO₂ for producing it is much less than in the case of hydrogenation-deoxygenation-type processes (HDO), with a consumption of at least 4 or 5% by weight of external hydrogen (according to the oxygen content of the feedstock).

[0076] The hydrogen of external origin can advantageously be supplied starting from fossil resources, by partial gasification/oxidation or by vapor reforming, by vapor-reforming of the bio-oil itself (although this involves a loss of energy efficiency of the carbon), by vapor reforming of the methane that is produced and light gas fractions and/or fractions comprising light oxygenated compounds that are obtained from the first hydroreforming stage or the subsequent hydrotreatment/hydrocracking stage. It is also possible to make the CO that is recovered react with the water that is produced to obtain hydrogen by means of the known reaction for conversion of the gas into water by "water gas shift" according to English terminology (WGS). Thus, the overall process, from the biomass to the final hydrocarbon-containing product, could be self-sufficient in hydrogen.

[0077] During the first hydroreforming stage, a moderate amount of gaseous hydrocarbon, essentially methane, is formed. This methane fraction can advantageously be reformed by means of the so-called steam methane reforming (SMR) for the purpose of producing bio-hydrogen for stages of hydroreforming or hydrotreatment and/or hydrocracking.

[0078] It is also possible to use bio-coal obtained from the pyrolysis stage as a feedstock for the gasification reactor for the purpose of producing synthetic gas (CO+H₂). This synthetic gas can also be used for producing bio-hydrogen for stages of hydroreforming or hydrotreatment and/or hydrocracking.

[0079] Thus, by implementing the SMR process and/or gasification of bio-coal, the process for converting and upgrading the bio-oil can be self-sufficient in hydrogen, without requiring the supply of hydrogen of fossil origin.

[0080] We have furthermore discovered that the partially deoxygenated bio-oil and more particularly the organic phase comprising at least said partially deoxygenated bio-oil that is produced by hydroreforming can be converted into aromatic compounds.

[0081] Hydrotreatment Stage

[0082] In accordance with the invention, at least one portion and preferably all of the organic phase of the effluent that is obtained from the first hydroreforming stage is sent into said second hydrotreatment stage in the presence of hydrogen in at least one reactor that contains a hydrotreatment catalyst, operating at a temperature of between 250 and 400° C., preferably between 320 and 380° C., at a pressure of between 2 MPa and 25 MPa, preferably between 5 MPa and 20 MPa, and at a hourly volumetric flow rate of between 0.1 h⁻¹ and 20 h⁻¹

and preferably between 0.5 h⁻¹ and 5 h⁻¹ and with a total amount of hydrogen mixed with the feedstock (including the chemical consumption and the recycled amount) such that the hydrogen/hydrocarbon volumetric ratio is between 100 and 3,000 Nm³/m³ and preferably between 100 and 1,000 Nm³/m³.

[0083] Said hydrotreatment catalyst advantageously comprises an active phase that comprises at least one metal of group 6 that is selected from among molybdenum and tungsten by itself or in a mixture, preferably combined with at least one metal of groups 8 to 10, preferably selected from among nickel and cobalt, by itself or in a mixture, and a substrate that is selected from the group that consists of alumina, silica, silica-alumina, magnesia, clays and mixtures of at least two of these minerals. Said substrate can also contain other compounds such as, for example, oxides that are selected from the group that consists of boron oxide, zirconia, titanium oxide, and phosphoric anhydride. In a preferred manner, said substrate consists of alumina, and preferably also [eta-], [theta-], [delta-] or [gamma-]alumina.

[0084] The total amount of metal oxides of group 6 and groups 8 to 10 in the hydrotreatment catalyst that is used is advantageously between 5 and 40% by weight, preferably between 6 and 35% by weight relative to the total catalyst mass. In the case where said catalyst comprises nickel, the nickel oxide content is advantageously between 0.5 and 12% by weight and preferably between 1 and 10% by weight relative to the total catalyst mass. In the case where the catalyst comprises molybdenum, the molybdenum oxide content is advantageously between 1 and 35% by weight of molybdenum oxide (MoO₃) and preferably between 5 and 30% by weight of molybdenum oxide, with these percentages being expressed in terms of % by weight relative to the total catalyst mass. A preferred catalyst is advantageously selected from among the catalysts NiMo, NiW or CoMo on an alumina substrate.

[0085] Said catalyst that is used in the second hydrotreatment stage can also advantageously contain at least one doping element that is selected from among phosphorus and boron. Said element can advantageously be introduced into the matrix, or, preferably, deposited on the substrate. It is also possible to deposit the silicon on the substrate, by itself or with phosphorus and/or boron. The oxide content in said element is advantageously less than 20%, and preferably less than 10% relative to the total catalyst mass.

[0086] The metals of the catalysts that are used in the second hydrotreatment stage of the method according to the invention can be metals or sulfur-containing metal phases. For maximum efficiency, these metal-oxide-based catalysts are usually converted at least partially into metal sulfides. The metal-oxide-based catalysts can be sulfurized by means of any technique that is known in the prior art, for example in the reactor (in-situ) or ex-situ, by putting the catalyst into contact, at an elevated temperature, with a hydrogen sulfide source, such as dimethyl disulfide (DMDS).

[0087] To the extent that the biomass normally contains only a very small amount of sulfur, the use of non-sulfur-containing catalysts should make it possible to avoid any risk of sulfur contamination in the fuels that are produced. Among the other metal-oxide-based catalysts that are suitable for the hydrotreatment stage, it is possible to cite the metal phases that are obtained by reduction under hydrogen. The reduction is done in general at temperatures of between approximately

150° C. and approximately 650° C., under a hydrogen pressure of between approximately 0.1 and approximately 25 MPa (14.5-3,625 psi).

[0088] Optional Separation

[0089] One stage for separation of at least one organic phase, at least one aqueous phase, and at least one gaseous phase can optionally be implemented between said second hydrotreatment stage and said third hydrocracking stage.

[0090] Said separation stage can advantageously be carried out by methods that are well known to one skilled in the art, such as the flash, distillation, stripping, liquid/liquid extraction methods, etc.

[0091] Nitrogen-containing, oxygenated and sulfur-containing impurities are removed from the organic phase that is obtained from the second hydrotreatment stage and optionally separated.

[0092] According to one variant of the invention, said organic phase that is optionally separated can also be fractionated in a fractionation zone into at least one light fraction that has an initial boiling point that is higher than 70° C. or higher than 80° C., and a final boiling point that is lower than 160° C. or lower than 170° C. or lower than 180° C., and into at least one heavy fraction that boils at a temperature that is higher than 160° C. or higher than 170° C. or higher than 180° C.

[0093] In this variant, said heavy fraction that boils at a temperature that is higher than 160° C. or higher than 170° C. or higher than 180° C. is preferably sent into said third hydrocracking stage of the process according to the invention, and said light fraction is preferably sent directly into the fourth stage of catalytic reforming, mixed with the fraction that contains naphtha separated at the end of said third hydrocracking stage.

[0094] The fractionation zone preferably comprises a fractionation cross-section that integrates a high-pressure high-temperature (HPHT) separator, and then atmospheric distillation.

[0095] Hydrocracking Stage

[0096] In accordance with the invention, at least one portion of the effluent that is obtained from the second hydrotreatment stage, and preferably at least one portion, in a preferred manner all of the organic phase of the effluent that is obtained from said optionally separated second hydrotreatment stage, mixed with a recycling of at least one portion and preferably all of the boiling fraction at a temperature that is higher than 160° C. separated at the end of a third hydrocracking stage, is sent into said third hydrocracking stage in the presence of hydrogen in at least one reactor that contains a hydrocracking catalyst, operating at a temperature of between 250 and 480° C., under a pressure of between 2 and 25 MPa, at a volumetric flow rate of between 0.1 and 20 h⁻¹, and with an amount of hydrogen that is introduced such that the hydrogen to hydrocarbon volumetric ratio is between 80 and 5,000 Nm³/m³.

[0097] Preferably, the feedstock of said third hydrocracking stage is the organic phase of the effluent that is obtained from the second hydrotreatment stage, optionally separated and/or fractionated.

[0098] The concatenation of said second hydrotreatment stage followed by the third hydrocracking stage of the process according to the invention of said third hydrocracking stage makes it possible to carry out, on the one hand, a rigorous hydrocracking so as to obtain a high fraction yield as well as a very deep hydrotreatment that makes it possible to obtain a

naphthenic fraction that is pure enough in terms of impurities to not poison the catalysts of catalytic reforming.

[0099] Hydrocracking is defined as hydrocracking reactions accompanied by hydrotreatment reactions (hydrodenitration, hydrodesulfurization), hydroisomerization, hydrogenation of aromatic compounds and opening of naphthene rings.

[0100] The hydrocracking stage according to the invention operates in the presence of hydrogen and a catalyst at a temperature of preferably between 320 and 450° C., in a preferred manner between 350 and 435° C., under a pressure of between 3 and 20 MPa, at a volumetric flow rate of between 0.1 and 6 h⁻¹, in a preferred manner between 0.2 and 3 h⁻¹, and with an amount of hydrogen that is introduced such that the volumetric ratio of hydrogen to hydrocarbons is between 100 and 3,000 Nm³/m³.

[0101] In accordance with the invention, at least one portion of and preferably all of the fraction that boils at a temperature that is higher than 160° C., preferably higher than 170° C., and in a preferred manner higher than 180° C., separated at the end of the third hydrocracking stage, is recycled in said third stage.

[0102] These operating conditions that are used in said third hydrocracking stage make it possible to obtain a high yield of naphtha fraction boiling at a temperature that is lower than 160° C. Said operating conditions make it possible to attain conversions per pass of the products having boiling points that are higher than 160° C., preferably higher than 170° C., and in a preferred manner higher than 180° C. into lighter products, higher than 30% by weight, in a preferred manner between 50 and 100% by weight, and in a very preferred manner between 70 and 100% by weight. The conversion per pass of products having boiling points that are higher than 160° C. into lighter products are defined as being: (mass of 160° C.+in the feedstock entering into said stage-mass of 160° C.+in the effluent existing from said stage)/(mass of 160° C. in the feedstock entering into said stage).

[0103] Said second hydrotreatment stage and said third hydrocracking stage can advantageously be carried out in a fixed-bed reactor or in a so-called entrained-bed: moving-bed reactor, boiling-bed reactor or suspension reactor. It is possible to use a single catalyst or several different catalysts, simultaneously or successively, in the case of a fixed-bed reactor. Said stages can be carried out industrially in one or more reactors, with one or more catalytic beds. The reaction exothermy during hydrotreatment is limited by any method that is known to one skilled in the art: recycling of the liquid product, cooling by recycled hydrogen, etc.

[0104] Said third hydrocracking stage according to the invention is preferably carried out in a so-called two-stage diagram, for maximizing the naphtha yield, optionally combined in an optional manner with a conventional hydrotreatment catalyst located upstream from the hydrocracking catalyst. The so-called two-stage hydrocracking diagram is widely known in the prior art.

[0105] The hydrocracking catalysts that are used in the third hydrocracking stage are all of the bifunctional type combining an acid function with a hydrogenating function. The acid function is provided by substrates whose surface areas in general vary from 150 to 800 m²/g and that have a surface acidity, such as halogenated aluminas (chlorinated or fluorinated, in particular), the combinations of boron and aluminum oxides, amorphous silica-aluminas and zeolites. The hydrogenating function is provided either by one or more

metals of group 6 of the periodic table, or by a combination of at least one metal of group 6 of the periodic table and at least one metal of groups 8 to 10.

[0106] Said hydrocracking catalyst can advantageously comprise metals of groups 8 to 10, preferably selected from among nickel and cobalt, preferably combined with at least one metal of group 6, selected from among molybdenum and tungsten and a substrate. The element content of groups 8 to 10 is advantageously between 0.5 to 20% by weight of oxide, and the element content of group 6 is advantageously between 1 to 40% by weight of oxide, preferably between 5 to 30% by weight relative to the total mass of said catalyst. The total content of metal oxides of groups 6 and 8 to 10 in the catalyst is generally between 5 and 40% by weight relative to the total mass of said catalyst. In the case where the catalyst comprises at least one metal of group 6 in combination with at least one non-noble metal of groups 8 to 10, said catalyst is preferably a sulfur-containing catalyst.

[0107] The hydrocracking catalyst can also contain a promoter element that is selected from among phosphorus, silicon and boron. This element may have been introduced into the matrix or preferably have been deposited on the substrate. The concentration of said element is usually less than 20% by weight (on the basis of oxide) and most often less than 10% relative to the total mass of said catalyst. When boron trioxide (B_2O_3) is present, its concentration is less than 10% by weight.

[0108] In an advantageous manner, the hydrocracking catalyst is selected from among the catalysts that comprise the following combinations of metals: NiMo, CoMo, NiW, CoW, NiMoP, and preferably NiMo, NiW, NiMoWP and NiMoP, and in an even preferred manner NiMoP.

[0109] Said hydrocracking catalyst advantageously comprises a substrate that is selected from the group that is formed by alumina, silica, silica-aluminas, zeolites, magnesia, clays and the mixtures of at least two of these minerals. This substrate can also contain other compounds and, for example, oxides that are selected from among boron oxide, zirconia, titanium oxide, and phosphoric anhydride.

[0110] Preferably, the substrate of said catalyst comprises at least one zeolite and in a preferred manner an FAU-structural-type Y zeolite, so as to maximize the yield in hydrocracking naphtha and then ultimately in aromatic compounds after catalytic reforming of said naphtha.

[0111] Preferably, the hydrocracking catalyst comprises a Y zeolite content of between 2 and 40% by weight and preferably between 10 and 35% by weight relative to the total mass of said catalyst.

[0112] Other preferred catalysts are so-called composite catalysts and comprise at least one hydrogenating-dehydrogenating element that is selected from the group that is formed by the elements of group 6 and groups 8 to 10 and a substrate based on a silica-aluminum matrix and based on at least one zeolite as described in the application EP1711260.

[0113] Prior to the injection of the feedstock, the catalysts that are used in the process according to this invention are preferably subjected to a sulfurization treatment (in-situ or ex-situ).

[0114] Separation

[0115] In accordance with the invention, the effluent that is obtained at the end of the third hydrocracking stage undergoes at least one separation stage so as to recover at least one fraction that contains naphtha and a fraction that boils at a temperature that is higher than 160° C., and preferably higher

than 180° C. The fraction that contains naphtha is defined as being a fraction that boils at a temperature that is lower than 160° C. and preferably lower than 180° C.

[0116] In accordance with the invention, at least one portion of the fraction that boils at a temperature that is higher than 160° C., preferably higher than 170, and in a preferred manner higher than 180° C., is recycled in said third hydrocracking stage. Preferably, the entirety of said fraction is recycled in such a way as to maximize the naphtha fraction yield. Said fraction is therefore recycled until used up in said third hydrocracking stage. In the case where the entirety of said fraction is recycled, a purging can advantageously be implemented.

[0117] The separation stage can advantageously be carried out by methods that are well known to one skilled in the art, such as the flash, distillation, stripping, liquid/liquid extraction methods, etc. It preferably comprises a fractionation cross-section that integrates a high-pressure high-temperature (HPHT) separator and then an atmospheric distillation.

[0118] A gaseous fraction can also advantageously be separated. Said gaseous fraction can then be advantageously treated in a hydrogen purification unit. The recovered hydrogen is advantageously recycled in said second hydrocracking stage and/or in said first hydrotreating stage. The gases containing undesirable nitrogen-containing, sulfur-containing and oxygenated compounds are evacuated.

[0119] The fraction that contains naphtha can optionally be separated into a light naphtha fraction (C5-C6) having a boiling point that is lower than 80° C. and preferably lower than 70° C. that is preferably at least in part subjected to an isomerization process for producing isomerate (basis for highway gasoline) and a heavy naphtha fraction that has an initial boiling point that is higher than 70° C. or 80° C., and a final boiling point that is lower than 160° C., or 170° C., or 180° C. Said heavy naphtha fraction is at least in part and preferably entirely subjected to the catalytic reforming stage for producing a reformat that is rich in aromatic compounds. The isomerization processes are widely known in the prior art; the isomerization makes it possible to transform a linear paraffin into isomerized paraffin for the purpose of increasing its octane number.

[0120] In one variant, said fraction that contains naphtha is sent in its entirety into the third catalytic reforming stage, without preliminary separation.

[0121] The fraction that contains the naphtha that is obtained after separation of the hydrocracking effluent has a strong naphthene content and very few impurities owing to rigorous hydrocracking. It is thus a particularly well suited feedstock for catalytic reforming.

[0122] Catalytic Reforming

[0123] In accordance with the invention, the fraction that contains naphtha that is obtained from the separation is sent into a fourth catalytic reforming stage that makes it possible to obtain hydrogen and a reformat that contains aromatic compounds.

[0124] The chemical reactions involved in the reforming stage are numerous. They are well known; for reactions beneficial to the formation of aromatic compounds, it is possible to cite: the dehydrogenation of naphthenes, the isomerization of cyclopentane rings, isomerization of paraffins, dehydrocyclization of paraffins, and for negative reactions, hydrogenolysis and hydrocracking of paraffins and naphthenes. Likewise, it is known that the catalysts of catalytic reforming

are particularly sensitive to poisoning that can be caused by metal impurities, sulfur, nitrogen, water and halides.

[0125] The catalytic reforming stage can be carried out, according to the invention, according to any one of the known processes, using any one of the known catalysts, and it is not limited to a particular process or catalyst. Numerous patents deal with processes for reforming or production of aromatic compounds with continuous or sequential regeneration of the catalyst.

[0126] The process diagrams in general use at least two reactors, in which a catalyst moving bed—through which a feedstock that consists of hydrocarbons and hydrogen passes, a feedstock heated between each reactor—circulates from top to bottom. Other process diagrams use fixed-bed reactors.

[0127] The continuous process for catalytic reforming of hydrocarbons is a process that is known to one skilled in the art; it makes use of a reaction zone that comprises a series of 3 or 4 reactors in series, working in a moving bed, and has a zone for regeneration of the catalyst that itself comprises a certain number of stages, including a stage for combustion of coke deposited on the catalyst in the reaction zone, an oxy-chlorination stage, and a final stage for reduction of the catalyst with hydrogen. After the regeneration zone, the catalyst is reintroduced at the top of the first reactor of the reaction zone. This process is described in, for example, the application FR2801604 or else FR2946660.

[0128] Said fourth stage of catalytic reforming advantageously operates under a pressure of between 0.1 and 4 MPa and preferably between 0.3 and 1.5 MPa, at a temperature of between 400 and 700° C., and preferably between 430 and 550° C., at a volumetric flow rate of between 0.1 and 10 h⁻¹ and preferably between 1 and 4 h⁻¹, and with a, preferably recycled, hydrogen/hydrocarbon ratio (mol.) of 0.1 to 10 and preferably between 1 to 5, and more particularly 2 to 4.

[0129] The catalyst that is used in said catalytic reforming stage advantageously comprises a substrate that is selected from among the refractory oxides and the zeolites and at least one noble metal that is selected from among platinum and palladium, and preferably at least one promoter metal that is selected from among tin and rhenium, at least one halogen, and optionally one or more additional elements that are selected from among alkalines, alkaline-earths, lanthanides, silicon, elements of group IV B, non-noble metals, and elements of group III A. These catalysts are extensively described in the literature.

[0130] Said catalytic reforming stage makes it possible to obtain a reformate that comprises at least 70% of aromatic compounds comprising a number of carbon atoms of between 6 and 11 relative to the total reformate mass. The conversion in general exceeds 80%.

[0131] The hydrogen that is produced in the catalytic reforming stage is preferably recycled in the first hydrotreating stage and/or in the second hydrotreating stage and the third hydrocracking stage.

[0132] Separation of Aromatic Compounds of the Reformate

[0133] In accordance with the invention, the aromatic compounds are separated from the reformate that is obtained at the end of the catalytic reforming stage.

[0134] Said stage for separation of the aromatic compounds contained in the reformate can advantageously be used by any method that is known to one skilled in the art. Preferably, it is

carried out by liquid-liquid extraction, extractive distillation, adsorption and/or crystallization. These processes are known by one skilled in the art.

[0135] The liquid-liquid extraction makes it possible to extract the aromatic compounds in the solvent constituting the extract. The paraffinic or naphthenic fractions are insoluble in solvent. In general, solvents are used such as sulfolane, N-methyl-2-pyrrolidone (NMP) or dimethyl sulfoxide (DMSO).

[0136] The primary extractive agents used in the extractive distillation are N-methyl-2-pyrrolidone (NMP), n-formylmorpholine (NFM), and dimethylformamide (DMF).

[0137] In said separation stage, transalkylation stages advantageously can be used to maximize the BTX yield.

[0138] Thus, aromatic compounds, essentially of the BTX (benzene, toluene, xylenes and ethyl benzene) type, are obtained.

[0139] A fraction that contains the aromatic compounds that are heavier than the BTX, i.e., the C9+ aromatic compounds, can advantageously be separated and recycled in the reforming stage.

DESCRIPTION OF THE FIGURE

[0140] FIG. 1 illustrates a particular embodiment of the process according to the invention.

[0141] The bio-oil obtained from the rapid pyrolysis of the biomass is introduced via the pipe (1), mixed with hydrogen (3) and the organic phase (8) that is obtained from the hydrotreating stage, in the first hydrotreating zone (2). The liquid effluent that is obtained from the hydrotreating zone via the pipe (4) is introduced into a separator (5). A gaseous phase that for the most part contains CO₂, H₂S and C1-C4 light gases, such as, for example, methane, is separated via the pipe (7), and an aqueous phase is also separated via the pipe (6). An organic phase that contains partially deoxygenated bio-oil and hydrocarbons is drawn off via the pipe (8), and a portion of said organic phase is recycled in the hydrotreating zone. The non-recycled part of said organic phase is then sent into a second hydrotreatment zone (9). The effluent that is obtained from the second hydrotreatment stage is introduced via the pipe (10) into a separator. A gaseous phase (13), an aqueous phase (12), and an organic phase (14) are separated, and nitrogen-containing, oxygenated and sulfur-containing impurities are removed from the organic phase that is sent into a third hydrocracking stage in a hydrocracking zone (15), in the presence of hydrogen (3). The effluent that is obtained from the second hydrocracking stage via the pipe (16) is sent into a separator (17). A fraction that boils at a temperature that is higher than 160° C. is separated in the pipe (18) and recycled in the third hydrocracking stage upstream from the zone (15). A light naphtha fraction that boils at a temperature of less than 80° C. can also be separated in the pipe (20). A heavy naphtha fraction that has an initial boiling point that is higher than 70° C. or 80° C. and a final boiling point that is lower than 160° C. is separated in the pipe (19) and sent into a fourth catalytic reforming stage in the zone (23). The reformate that is obtained at the end of the catalytic reforming stage in the pipe (24) is then separated in the one separator (25). A fraction that contains the BTX aromatic compounds is separated in the pipe (26) and a fraction that contains the aromatic compounds that are heavier than the BTX, i.e., the C9+ aromatic compounds, is also separated in the pipe (27).

[0142] The examples below illustrate the invention without limiting its scope.

EXAMPLES

[0143] Experiments have been conducted with a bio-oil obtained by rapid pyrolysis of hardwood mixtures. The operating conditions of rapid pyrolysis are a temperature of 500° C. and a dwell time of the vapors on the order of one second. Table 1 below exhibits the data obtained following the analysis of this bio-oil.

TABLE 1

Analysis of Bio-Oil	
Density at 20° C., g/cm ³	1.21
Kinematic viscosity at 20° C., mm ² /s	182.6
pH	2.5
Higher calorific value, MJ/kg ^a	18.03
Lower calorific value, MJ/kg ^b	16.46
Water content, % by mass	20.7
Pyrolytic lignin, % by mass	19.0
Carbon, % by mass	43.9
Hydrogen, % by mass	7.39
Nitrogen, % by mass	<0.05
Oxygen, % by mass	47.3
Sulfur (ppm)	92

^aThe higher calorific value is measured with a calorimetric bomb.

^bThe lower calorific value is calculated by means of the following equation: LHV (J/g) = HHV (J/g) – 218.13 * H % (% by weight)

Example 1

Preparation of C1 Hydroreforming Catalysts

[0144] The C1 catalyst is a catalyst of formulation NiCr/C. The precursors of nickel and chromium, in their nitrate form (respectively Ni(NO₃)₂ and Cr(NO₃)₃), are provided by Aldrich. The substrate is an activated carbon in the form of cylindrical extrudate provided by the Norit Company (RX3 Extra). This C1 catalyst is obtained by dry impregnation with an aqueous solution that contains the precursors of nickel and chromium. The solution volume is equal to the volume of water uptake of the substrate (i.e., the maximum water volume that can penetrate into its porosity). The concentrations of nickel and chromium precursors in solution are determined in such a way as to obtain the target contents on the final catalyst: 10% by weight of nickel and 5% by weight of chromium. After impregnation of this aqueous solution, the catalyst is allowed to mature at ambient temperature for 4 hours in a water-saturated chamber and then dried in an oven at 70° C. in air for 3 hours and finally undergoes a heat treatment at 300° C. for 3 hours under nitrogen (at a flow rate of 1.5 L/h/g of catalyst).

TABLE 1

Formulation of the C1 Catalyst.	
Catalyst	C1
Substrate	Activated Carbon
Ni (% by Weight)	10.2
Cr (% by Weight)	4.9
Mo (% by Weight)	—

Example 2

Production of a Reformate that Contains More than 70% by Weight of Aromatic Compounds from a Non-Pretreated Bio-Oil

[0145] This example illustrates the production of an oxygen-free reformate that contains more than 70% by weight of BTX aromatic compounds from the treatment of a non-pretreated bio-oil liquid feedstock with the characteristics that are described in Table 1, according to the process of the invention.

[0146] For the first hydroreforming stage, the non-pretreated bio-oil is first introduced, mixed with an organic liquid phase that is obtained from the hydroreforming stage, according to a 1:3 ratio (organic liquid phase:bio-oil) simulating a recycling rate of 0.33, in the autoclave reactor with a hydroreforming catalyst.

[0147] 15 g of C1 catalyst prepared according to Example 1 is reduced in a reduction cell at 300° C. for 3 hours in 30 NL/h of hydrogen and then introduced, in a glove bag under inert atmosphere, into a basket that is placed in the autoclave reactor with 75 g of bio-oil and 25 g of the organic liquid phase that is obtained from the hydroreforming stage. The reactor is closed in an airtight way and purged with nitrogen and then with hydrogen. The reactor is then put under pressure at 4.83 MPa (700 psia) with 18.37 NL of H₂, and then gradually heated while being stirred at 330° C. and kept at this temperature for 3 hours during which the maximum pressure reached was 13.9 MPa (2,016 psia). The equivalent volumetric flow rate, defined as the ratio of the bio-oil volume introduced into the product of the catalyst volume by the test duration, is equal to 0.7 h⁻¹. The reactor is then quickly cooled and brought to ambient temperature, which brings the pressure to 1.17 MPa (170 psia). The reaction gas phase that is produced, 4.9 NL in all, is sent into a collecting bottle and analyzed. Analysis by gas phase chromatography indicates that it contains 63.9% H₂, 21.6% CO₂, 10.6% CH₄, and 3.0% CO by volume.

[0148] The basket that contains the catalyst is recovered outside of the liquid that is produced, which is separated into 50.33 g of a higher homogeneous organic liquid oil phase with a density of 980 kg/m³ and 38.37 g of a lower aqueous phase. No deposit of tar is observed in the reactor. The organic liquid phase contains 13.93% by weight of elementary oxygen and 4.68% by weight of water, (2.36 g) of water, determined by elementary analysis and Karl-Fischer metering.

[0149] The overall net consumption of hydrogen rises to 15.26 NL (1.39 g), which corresponds to approximately 1.85% by weight relative to the bio-oil mass that is introduced. Starting from data above, the yields of organic liquid phase and aqueous phase are determined at 38.5% and 29.4% by weight respectively, relative to the bio-oil, or 27.8% and 21.2% by weight, respectively, on the basis of the dry biomass containing 0% moisture.

[0150] The organic liquid phase that is obtained from the hydroreforming stage is then sent into a flushed fixed-bed reactor in the presence of a conventional hydrotreatment catalyst for a hydrotreatment stage (HDT). The hydrotreatment catalyst that is used comprises 4.3% by weight of NiO, 21% by weight of MoO₃, and 5% by weight of P₂O₅, supported on a gamma-alumina. Prior to the test, this catalyst is sulfurized in-situ at a temperature of 350° C., using a feedstock that contains the additive heptane of 2% by weight of dimethyl disulfide (DMDS).

[0151] 25 mL/h of the organic liquid phase obtained from the hydrotreating stage is introduced into an isothermal reactor and with a fixed bed that is charged with 25 ml of hydrotreating catalyst. The corresponding volumetric flow rate is equal to 1 h^{-1} . 800 Nm^3 of hydrogen/ m^3 of feedstock is introduced into the reactor that is kept at a temperature of 320°C . and at a pressure of 10 MPa (1,450 psia). So as to keep the catalyst in the sulfur state, 50 ppm by weight of sulfur in the form of DMDS is added to the feedstock. Under the reaction conditions, the DMDS is totally broken down for forming methane and H_2S .

[0152] At the end of 1 hour of operation of the test, 19.63 g of a hydrocarbon liquid phase with a density of 842 kg/m^3 , containing 0.12% by weight of water, 0.2% by weight of elementary oxygen (quantification limit of the analyst) and 99.7% by weight of hydrocarbons, has been recovered. The net hydrogen consumption corresponds to 2.2% by weight relative to the mass of organic effluent that is sent to the hydrotreating stage, which corresponds to a net hydrogen consumption of 0.9% by weight relative to the bio-oil. The overall yield of hydrocarbon-containing liquid is equal to 29.7% by weight relative to the bio-oil or 21.4% by weight on the basis of dry biomass.

[0153] The hydrocarbon-containing liquid that is obtained from the hydrotreating stage is then sent into a flushed fixed-bed reactor in the presence of a hydrocracking catalyst that simulates the conversion reactor for the hydrocracking stage. The hydrocracking catalyst that is used comprises 3.3% by weight of NiO, 16% by weight of MoO_3 , and 3.8% by weight of P_2O_5 supported on a commercial Y zeolite of reference CBV 712 mixed with a gamma-alumina in a mass ratio of 1:4 (zeolite mass:alumina mass). Said catalyst is sulfurized.

[0154] 25 mL/h of hydrocarbon-containing liquid that is obtained from the hydrotreating stage is introduced into an isothermal reactor and with a fixed bed charged with 25 mL of hydrocracking catalyst. The corresponding volumetric flow rate is equal to 1 h^{-1} . $1,000 \text{ Nm}^3$ of hydrogen/ m^3 of feedstock is introduced into the reactor that is kept at a temperature of 380°C . and a pressure of 12 MPa (1,740 psia). The effluent that is recovered at the outlet of the reactor is cooled, flashed, and fractionated into three distillation fractions: PI- 80°C ., $80\text{-}180^\circ \text{C}$. and 180°C +. The PI- 80°C . and $80\text{-}180^\circ \text{C}$. fractions are recovered, and the 180°C +. fraction is recycled in a continuous way at the inlet of the reactor. The conversion per pass of products having boiling points of higher than 180°C . of product having a boiling point of less than 180°C . is estimated at 50%. The overall yield of the naphtha fraction having boiling points of between 80 and 180°C . is equal to 22.5% by weight relative to the bio-oil or 16.2% by weight on the basis of the dry biomass.

[0155] The $80\text{-}180^\circ \text{C}$. naphtha fraction is then sent into a flushed fixed-bed reactor in the presence of a reforming catalyst. The reforming catalyst that is used comprises 0.3% by weight of platinum, 0.3% by weight of tin, and 1.0% by weight of chlorine supported on a gamma-alumina. The catalytic reforming stage was carried out in continuous mode in a fixed-bed reactor with 2.5 g of catalyst at 520°C ., a total pressure of 0.9 MPa, an H_2/HC ratio of 1.7, and a WHSV of 2 h^{-1} . The catalyst is first reduced in-situ at 500°C . for 2 hours. The product at the outlet of the reactor is cooled, recovered, and an aliquot is analyzed by gas chromatography for determining the contents of benzene, toluene and xylene aromatic compounds. 3.6% by weight of hydrogen relative to

the mass flow rate of the feedstock that is introduced into the reforming reactor is generated. The overall yield of reformat is equal to 91% by weight relative to the feedstock that is introduced or 20.5% by weight relative to the bio-oil or 14.7% by weight on the basis of the dry biomass. The reformat contains 3.1% by weight of benzene, 13.0% by weight of toluene, 23.2% by weight of xylene, 27.4% by weight of C9 aromatic compounds, and 9.4% by weight of C10 aromatic compounds. The overall yield of total aromatic compounds and BTX represents, respectively, 15.6% by weight and 8.1% by weight relative to the bio-oil or 11.2% by weight and 5.8% by weight relative to the dry biomass.

[0156] These results show that a reformat that contains more than 70% by weight of aromatic compounds and approximately 40% by weight of BTX (measured by gas phase chromatography) can be obtained from the treatment of a non-pretreated bio-oil according to the concatenation of the hydrotreating/hydrotreatment/hydrocracking/catalytic reforming stages. This example does not integrate the aromatic complex making it possible to separate and to maximize the BTX yield.

[0157] The entire disclosures of all applications, patents and publications, cited herein and of corresponding application Ser. No. 12/01544 FR, filed May 30, 2012, are incorporated by reference herein.

1. Process for the production of aromatic compounds starting from a liquid feedstock that comprises at least one bio-oil, said feedstock being introduced into at least the following stages:

A first hydrotreating stage in the presence of hydrogen and a hydrotreating catalyst that comprises at least one transition metal that is selected from among the elements of groups 3 to 12 of the periodic table and at least one substrate that is selected from among activated carbons, silicon carbides, silicas, transition aluminas, alumina-silicas, zirconium oxide, cerium oxide, titanium oxide, and the aluminates of transition metals, taken by themselves or in a mixture, for obtaining at least one liquid effluent that comprises at least one aqueous phase and at least one organic phase,

A second stage for hydrotreatment of at least one portion of the organic phase of the effluent that is obtained from the first hydrotreating stage in the presence of hydrogen in at least one reactor that contains a hydrotreating catalyst, operating at a temperature of between 250 and 400°C ., at a pressure of between 2 MPa and 25 MPa, at an hourly volumetric flow rate of between 0.1 h^{-1} and 20 h^{-1} , and with a total amount of hydrogen mixed with the feedstock such that the hydrogen/hydrocarbon volumetric ratio is between 100 and $3,000 \text{ Nm}^3/\text{m}^3$,

A third hydrocracking stage of at least one portion of the effluent that is obtained from the second hydrotreatment stage, in the presence of hydrogen, in at least one reactor that contains a hydrocracking catalyst, operating at a temperature of between 250 and 480°C ., under a pressure of between 2 and 25 MPa, at a volumetric flow rate of between 0.1 and 20 h^{-1} , and with an amount of hydrogen that is introduced such that the hydrogen to hydrocarbon volumetric ratio is between 80 and $5,000 \text{ Nm}^3/\text{m}^3$, in which at least one portion of the fraction that boils at a temperature that is higher than 160°C . that is separated at the end of said third hydrocracking stage is recycled in said third hydrocracking stage,

A separation of the effluent that is obtained at the end of the third hydrocracking stage into at least one fraction that contains naphtha and a fraction that boils at a temperature that is higher than 160° C.,

A fourth stage for catalytic reforming of the fraction containing naphtha that is obtained from the separation operating in the presence of a catalytic reforming catalyst, under a pressure of between 0.1 and 4 MPa, at a temperature of between 400 and 700° C., at a volumetric flow rate of between 0.1 and 10 h⁻¹, and with a hydrogen/hydrocarbon ratio of 0.1 to 10, making it possible to obtain hydrogen and a reformat that contains aromatic compounds,

and a stage for separation of the aromatic compounds of the reformat obtained at the end of the catalytic reforming stage.

2. Process according to claim 1, in which said first hydroreforming stage is carried out at a temperature of between 250 and 450° C., and at an absolute pressure of between 3.4 and 27.6 MPa (500 and 4,000 psi), at a volumetric flow rate of between

0.5 h⁻¹ and 5 h⁻¹ relative to the bio-oil and with an amount of hydrogen that is introduced such that the volumetric ratio of hydrogen to hydrocarbons is between 50 and 2,000 Nm³/m³.

3. Process according to claim 1, in which said liquid feedstock comprising at least one bio-oil also contains other liquid feedstocks obtained from the biomass, with said liquid feedstocks being selected from among vegetable oils, alga or algal oils, fish oils, fats of vegetable or animal origin, and alcohols obtained from the fermenting of sugars of the biomass, or mixtures of such feedstocks, which may or may not be pre-treated.

4. Process according to claim 1, in which said liquid feedstock consists entirely of bio-oil.

5. Process according to claim 1, in which the hydroreforming catalysts comprise Ni, Cu, NiCr, NiMo or NiMn on activated carbon or on alumina or nickel aluminate.

6. Process according to claim 1, in which a stage for separation of at least one organic phase, at least one aqueous phase, and at least one gaseous phase can be carried out between said second hydrotreatment stage and said third hydrocracking stage.

7. Process according to claim 6, in which said organic phase is fractionated in a fractionation zone into at least one light fraction that boils at a temperature of between 80 and 160° C. and into at least one heavy fraction that boils at a temperature that is higher than 160° C.

8. Process according to claim 7, in which said heavy fraction that boils at a temperature that is higher than 160° C. is sent into said third hydrocracking stage and said light fraction is sent directly into the fourth catalytic reforming stage, mixed with the fraction that contains naphtha separated at the end of said third hydrocracking stage.

9. Process according to claim 1, in which said hydrocracking catalyst comprises metals of groups 8 to 10 that are selected from among nickel and cobalt, combined with at least one metal of group 6, selected from among molybdenum and tungsten and a substrate that is selected from among alumina, silica, silica-aluminas, zeolites, magnesia, clays, and the mixtures of at least two of these minerals.

10. Process according to claim 9, in which the substrate of said hydrocracking catalyst comprises at least one FAU-structural-type Y zeolite.

11. Process according to claim 1, in which the entire fraction that boils at a temperature that is higher than 160° C., separated at the end of the third hydrocracking stage, is recycled in said third stage.

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