

Description

Title of Invention: Production of halide free hydrocarbons

Technical Field

- [0001] This invention relates to a process and a system for conversion of a hydrocarbonaceous feed comprising halides and nitrogen, and specifically a cost-effective process and system for removing ammonium halides from a hydrocarbon stream comprising ammonia and one or more halides.

Background Art

- [0002] Refinery and petrochemical processes comprise a plurality of treatments of hydrocarbon rich streams in order to provide products or intermediates in the form of LPG, naphtha, gasoline, diesel, etc. to be used either as fuels or in the petrochemical industry. Such treatments comprise hydro-treatment, hydro-cracking, steam-cracking, fractionation and stripping, as well as intermediate heat exchange and removal of impurities.
- [0003] Hydrocarbonaceous feedstock may, depending on origin, contain heteroatoms, undesired in the downstream processing. The most abundant heteroatoms are sulfur, nitrogen and oxygen, which may be present in concentrations from 100 ppm_{wt} to 10 wt%, and for oxygen in some biological materials even as high as 45wt%. These heteroatoms are in refinery hydrotreatment processes converted into hydrogen sulfide, ammonia, water and carbon oxides, which cause few minor and well-known challenges in the process plants. Other heteroatoms are typically metals, which typically are present in small amounts (0-10 ppm_{wt}) and precipitate on catalyst guard particles, and thus also cause few challenges in the process plants. However, when treating biomass or waste products such as plastic waste, some heteroatoms may be present in much higher concentrations than in fossil feedstocks. For thermally decomposed waste, e.g. pyrolyzed plastic, the content of e.g. Cl may be 1000 ppm_{wt} or higher, and after hydrotreatment the organic Cl will have been converted to HCl which may cause corrosion issues, especially if the acidity of HCl is not neutralized. It is therefore important to remove the heteroatoms early in the process, to minimize the effect on down-stream process steps. Similar issues may also be observed for biomass comprising halides, e.g. if originating from salt water.
- [0004] In addition to halides notably nitrogen is also present in the hydrocarbonaceous feedstocks. During hydrotreatment organically bound nitrogen is converted to ammonia which may have the benefit of neutralizing HCl. However, ammonia and halides may react to form salts, e.g. ammonium chloride, which is a solid at temperatures below the precipitation temperature which typically is 150°C to 300°C. Pre-

precipitation of such salts may result in partial or complete blocking of process lines as well as potential corrosion and must therefore be avoided. Therefore, it is important to ensure the process temperature to be above the inorganic halide precipitation temperature.

- [0005] From 30% or 80% to 90% or 100% of the organic halides in a hydrocarbonaceous feedstock, may be converted to inorganic halides in a hydrocarbon product stream by one embodiment of the disclosure. The hydrocarbon product is washed with water which dissolves inorganic halides and ammonia and may be separated from the hydrocarbon stream.
- [0006] By the washing with water, the most or all of the inorganic halides from the hydrocarbon stream are removed from the product. These inorganic halides removed from the hydrocarbon stream may be taken away from the system in a dilute aqueous wash water solution, or e.g. by regenerating the wash water by evaporation, membrane separation, reverse osmosis or other means of concentrating the impurities in a brine.
- [0007] In the following a hydrocarbonaceous feedstock shall be used to signify a feedstock rich in molecules comprising hydrogen and carbon, but possibly also heteroatoms, i.e. other elements, such as halides, oxygen, sulfur and nitrogen.
- [0008] Where concentrations are stated in wt% this shall be understood as weight/weight %, and similarly ppm_w as parts per million by mass.
- [0009] Throughout this text, the term “a material catalytically active in conversion” (such as hydrotreatment) is meant to denote catalyst material arranged for and/or suitable for catalyzing the conversion to a commercially relevant extent.
- [0010] “Organic halides” are chemical compounds in which one or more carbon atoms are linked by covalent bonds with one or more halogen atoms (fluorine, chlorine, bromine, iodine or astatine – group 17 in the IUPAC periodic table of elements date 1 Dec 2018).
- [0011] “Inorganic halides” are chemical compounds comprising a halogen atom and an element or radical that is less electronegative (or more electropositive) than the halogen, to make a fluoride, chloride, bromide, iodide, or astatide compound, with the further limitation that carbon is not part of the compound.
- [0012] The term “removing halides” is meant to include situations where either some or all of the halides present in organic form are converted into inorganic halides, and subsequently removed. The term is thus, unless otherwise indicated, not limited to situation where a certain percentage of the halides present are removed.
- [0013] The term “conversion of organic halides to inorganic halides” shall refer to halides in organic compounds undergoing reaction, such that they are part of inorganic compounds. Quantification of such conversion shall be in terms of the moles of halides present in organic and inorganic compounds respectively.
- [0014] The term “react in the presence of the catalytically active material” is meant to cover

bringing a stream into contact with the catalytically active material under effective conditions for the implied catalytic reaction to take place. Such conditions typically relate to temperature, pressure and stream composition. A typical example of a material catalytically active would be a classical refinery hydrotreatment catalyst, such as one or more sulfided base metals on a refractive support.

[0015] The term “precipitation temperature” of ammonium halides is meant to cover the temperature (under the given conditions, such as concentration and pressure) at which gaseous ammonia and gaseous inorganic halides (typically hydrogen halides) precipitate, either by reacting to form solid ammonium halide crystals. For ammonium chloride in concentrations above 500 ppm_w and a pressure of 100 Barg this temperature is approximately 280°C as an example, and typically for the relevant conditions this temperature will be in the range 150-300°C.

[0016] The term “thermal decomposition” shall for convenience be used broadly for any decomposition process, in which a material is partially decomposed at elevated temperature (typically 250°C to 800°C or perhaps 1000°C), in the presence of substoichiometric amount of oxygen (including no oxygen). The product will typically be a combined liquid and gaseous stream, as well as an amount of solid char. The term shall be construed to include processes known as pyrolysis, partial combustion, or hydrothermal liquefaction.

[0017] The unit “Barg”, shall in compliance with the practice of the field be used to denote Bar, gauge, i.e. the pressure relative to atmospheric pressure and all pressures reported and compared shall be pressures relative to atmospheric pressure.

Solution to Problem

[0018] The process and the system disclosed may be found useful where the feed to a hydrotreatment process comprises halides. Examples of such feeds include the products of processes such as the product from thermal decomposition of halide rich materials, such as waste plastic, comprising e.g. PVC, other halide containing plastics, PTFE and similar materials and plastic comprising brominated flame retardants, alone or in mixed waste as well as of biological materials with high halide content, e.g. straw and algae, as well as other products of thermal decomposition or solothermal liquefaction processes using water or other solvents to aid the decomposition, kerogenic feeds such as coal tar or shale oil. The feed comprising halides may also originate from non-pyrolyzed renewable feedstocks, e.g. waste cooking oil, algae lipids, especially when grown in salt water, or other biological feeds comprising hydrocarbons, nitrogen and halides.

[0019] Ammonia and halides react to form salts, e.g. ammonium chloride, at temperatures below the precipitation temperature typically 150 °C to 300°C. Precipitation of such salts may result in partial or complete blocking of process lines as well as potential

corrosion and must therefore be avoided. Therefore, it is also relevant to be aware of this aspect when defining the process conditions.

- [0020] After the hydrotreatment of a halide containing hydrocarbonaceous feedstock, a mixed product stream rich in inorganic halides, will be present. Depending on the boiling range and the process temperature and pressure, the stream may be a one-phase gas stream or a two-phase stream with a gas phase rich in hydrogen and hydrogenated hetero-atoms, such as hydrogen chloride and ammonia and a liquid stream comprising mainly hydrocarbons. In the latter case, separating the two-phase stream and minimizing the amount of hydrogen halides in the liquid stream comprising hydrocarbons may put fewer demands to corrosion resistance in the choice of materials in process equipment handling this stream.
- [0021] As the hydrogenated hetero-atoms including the inorganic halides are water soluble, addition of an amount of wash water and cooling the stream, will result in a three-phase stream, comprising a gas phase, an organic non-polar phase and an aqueous polar phase, which may be separated in a so-called three-phase separator, possibly in combination with a cascade of separators with intermediate cooling and pressure release.
- [0022] If the hydrocarbonaceous feedstock comprises an amount of nitrogen, the mixed product stream from hydrotreatment would also comprise an amount of ammonia. Ammonia and halides may react to form ammonium halides, such as ammonium chloride, which is easily formed and which rapidly solidifies under the appropriate conditions, which are mainly dictated by a precipitation temperature, approximately corresponding to the sublimation temperature of the ammonium halide. The inorganic halide precipitation temperature is dependent on concentrations and pressure in accordance with well-known thermodynamic principles.
- [0023] In traditional refinery processes such a water washing process step is also seen, e.g. in the context of nitrogen rich hydrocarbons, which are converted to ammonia, which is highly soluble in water, and which enables withdrawal of hydrogen sulfide as ammonium bisulfide in the wash water. The concentration of nitrogen hetero-atoms may be above 1 wt%, and the mass ratio of water consumed to hydrocarbon to is typically 1:20 or 1:10, resulting in a concentration of ammonia salts in water around 1 wt% to 5 wt%. This design is commonly limited by the concentration of ammonium bisulfide; however, this concentration is allowed to be up to 2 wt% to 4 wt% before corrosion and deposition becomes an issue.
- [0024] In a process where halides are among the hetero-atoms of a hydrocarbonaceous feed, and where they are present in levels above 100 ppm_{wt}, it is however necessary to increase the amount of water in the washing process, to achieve quantitative withdrawal of halides from the non-polar phase, while avoiding corrosion issues from

elevated halide concentration in the water phase. With a feedstock comprising 500 ppm_{wt}Cl and a purified hydrocarbon comprising less than 1 ppm_{wt}Cl, the mass ratio of water to hydrocarbon may be about 1:1, as typical design limits requires keeping Cl levels in the water below 600 ppm_{wt}, which corresponds to the requirement for carbon steel or higher alloy steel depending on temperature and pH. This amount of water is 10 to 20 times higher than the normal practice in the refinery industry. If NH₃ or another base component is present in the stream, the pH will be higher, and the corrosion due to presence of Cl will be reduced, but the risk of salt precipitation will be increased.

- [0025] Such a high amount of wash water is of course an economical and environmental challenge, and therefore it is desirable to reduce the amount of water consumed. This may be done by providing a means of concentration of the used wash water, such that it is separated in purified wash water and a concentrated brine rich in impurities, such as halides. Multiple methods exist for this purpose, including membrane filtration, reverse osmosis or evaporation, including falling film evaporation. The equipment used in the evaporation process will be much more expensive if special grades of steel are required, so it is also beneficial to consider reducing the corrosiveness of the used wash water, e.g. by neutralizing the used wash water.
- [0026] To minimize presence of halides, the hydrocarbon stream must be purified to a high extent. This may be done by separating the mixed product stream in a high boiling hydrocarbon product, which only contains minor amounts of the inorganic gases ammonia or halides and a gaseous product stream comprising a high amount of the inorganic gases. Such a separation may be carried out in equipment of simple design, e.g. a flash drum. The purity of the high boiling hydrocarbon product will however be higher if a stripping medium is directed to the high boiling liquid hydrocarbon stream, to drive out any gases, and fractionation or stripping at low pressure may be required to release halides from the high boiling liquid hydrocarbon stream.
- [0027] To avoid precipitation of ammonium halides in or downstream the separation equipment it is necessary to operate the separation at an elevated temperature, above the precipitation temperature of the ammonium halides potentially formed from the ammonia and halides present in the stripper overhead stream, i.e. above 150-230°C or even higher, contrary to the regular operation especially of strippers in refinery plants, where they typically operate below or slightly above the boiling point of water, especially if the objective is to drive out gases. If the stripper is operated at the same (high) pressure as the process, it may be preferred to use hydrogen as the stripping medium, since hydrogen must be added as a reagent anyway, but carrying out a stripping process at elevated pressure, will reduce the separation efficiency, compared to a stripping process operated at low pressure. Therefore, additional hydrocarbons

may be recuperated from the stripper vapor by condensation, but the condensate stream may require stabilization by stripping off light gases.

[0028] Generating a liquid phase with a minimum of halides by efficiently stripping the halides immediately downstream hydrotreatment may be considered beneficial, since this may minimize the process equipment contacted by halides. However, as an alternative to a process where stripping is carried out immediately after reaction, at elevated pressure, we have now identified that a more cost effective process may be obtained by gas/liquid separation at high pressure and high temperature, such that a hot high boiling liquid with a moderate amount of halides and a sour gas phase are obtained. The sour gas phase may be washed, cooled and separated in a three phase separator, providing sour water, purified hydrogen rich gas and a light condensate. The light condensate and the high boiling liquid may comprise only non-corrosive amounts of halides from a processing perspective, but they will still be above specification limits. However, the temperature of the high boiling liquid is sufficiently high to allow depressurizing and stripping the halides from the high boiling liquid hydrocarbon stream e.g. with steam as stripping medium. The temperature of the light condensate is much lower, but halides may still be stripped from this stream at low pressure using steam or reboiled condensate heated by the purified high boiling liquid hydrocarbons. In addition, the proposed process also has the benefit that stripping at low pressure is more efficient and the low pressure equipment has a lower cost.

[0029] Such a scheme may also provide additional benefits, including a reduced amount of the sour gas phase, as it will not contain hydrogen stripping medium nor stripped off light hydrocarbons. As a consequence, the amount of wash water required in the high pressure section may also be reduced.

[0030] The product of the process may be directed to further treatment, either for the production of hydrocarbon transportation fuel or for petrochemical processes, i.e. in a steam-cracker. If the product of the process is intended for the production of hydrocarbon transportation fuel it may be desirable to provide additional steps of hydroprocessing, such as hydrocracking, either in the same high pressure loop as the hydrotreatment or after the separation in a separate high pressure loop.

Brief Description of Drawings

[0031] [Fig.1] discloses a system for treating hydrocarbons employing a hot separator and two low pressure strippers.

[0032] [Fig.2] discloses a system for treating hydrocarbons employing a hot pressure stripper, a fractionator and a stabilizer according to the prior art.

[0033] Even though some heat exchange units, pumps and compressors are shown in the figures, further pumps, heaters, valves and other process equipment may be part of the

system shown in the figures, and similarly some of the equipment shown may be omitted or implemented differently in practice.

Fig.1

- [0034] [Fig.1] shows a feedstock stream (102) containing a halide such as chlorine. This stream is optionally preheated, before being combined with a hydrogen rich gas stream (104) to a hydrogen enriched feedstock stream (106) in order to ensure the provision of the required hydrogen for the hydrogenation of di-olefins in first reactor (DOR). The hydrogen enriched feedstock stream (106) may optionally have been heated in one or both of a heat exchanger (shown) and other heating such as a fired or electrical heater (not shown) to provide sufficient temperature for activating the hydrogenation of di-olefins. The first reactor (DOR) is optional but may have operating conditions at a pressure of 30 Barg to 150 Barg and a temperature of about 180°C, such as 150°C to 220°C, suitable for hydrogenation of di-olefins. The first reactor (DOR) may contain a material catalytically active in di-olefin saturation and hydro-dehalogenation. Within this first reactor (DOR), the hydrogen enriched hydrocarbon stream (106) would react in the presence of the catalytically active material, rendering a first hydrogenated product stream (108), which here is combined with an optional recycled hydrocarbon stream (110) which is heated, e.g. by heat exchange and the combined hydrogenated feed stream (112) is directed to a guard reactor (GRD) in which reactive heteroatoms react such that impurities are captured in a material catalytically active in hydrotreatment. The purified feedstock (114) is here heated further in a charge heater (CH) and directed to hydrotreatment in a hydrotreatment reactor (HDT) in which further heteroatoms such as nitrogen, sulfur, oxygen and halides are released as gaseous inorganic hydrogen compounds in a mixed gas/liquid stream of hydrotreated intermediate, which is cooled by heat exchange – here with the combined hydrogenated feed stream (112) and by heat exchange with a heat exchange medium (120) – here in a boiler with a stream of boiler feed water producing steam – for heating the hydrogen enriched feedstock stream (106).
- [0035] The mixed gas/liquid stream of hydrotreated intermediate (116) is after cooling directed to a high pressure hot separator operating at above the precipitation temperature of ammonium halides in the mixed gas/liquid stream such as around 290 °C, from which a liquid hydrotreated intermediate (122) and a mixed gas stream (124) are withdrawn. The mixed gas stream (124) is combined with wash water (126) and the combined gas/water stream (128) is after cooling directed to a high pressure cold separator (HPCS), to separate the product in three phases; a recycle gas (130), which (optionally after further purification) is pressurized in recycle gas compressor (RCGC) and combined with make-up hydrogen gas (132) and directed as the hydrogen rich gas (104); a sour water (134) which is directed to cleaning possibly involving separation of

an amount of the water for reuse as wash water and finally a condensate product (136).

[0036] The liquid hydrotreated intermediate (122) and the condensate product (136) are depressurized to a pressure from slightly above atmospheric pressure to 15 barg and directed to a final purification stage. The liquid hydrotreated intermediate (122) is maintained at an elevated temperature after the hot separator and may therefore be directed to a high temperature stripper (HTST) operating with steam as stripping medium (138). Due to the high temperature of the liquid hydrotreated intermediate (122), it is not required to use a fired heater as the heat source for reboiling, and instead steam may be used as stripping medium (138), since the stripper vapor (146) may be maintained above the inorganic halide precipitation temperature, possibly even if the steam temperature is as low as 200°C. The condensate is directed to a low temperature stripper (LTST) providing a low temperature stripper vapor (142), which must be above the inorganic halide precipitation temperature, and a purified condensate (144). The purified condensate (144) is reboiled by heat exchange with the stripped liquid hydrotreated intermediate (140), by heat exchange with steam or reboiled by other means or alternatively stripped with added steam. The low temperature stripper vapor (142) and the high temperature stripper vapor (146) both may contain some hydrogen halides, and are therefore combined with a further amount of wash water (148) and the combined water/stripper vapor stream (152) is after cooling directed to an overhead separator (OSEP) in which sour water (154) and stripper reflux (156) are condensed and separated from off-gas (158). Optionally the off-gas (158) may be contacted with a liquid hydrocarbon (160) here an amount of the purified condensate (144) in a recontact drum (CONT) to capture liquid hydrocarbons in a recycle liquid stream (162) and provide an off-gas (164) with minimal amounts of hydrocarbons. The stripped liquid hydrotreated intermediate (140) – optionally after separation of water in a coalescer (CLSC) or a drier - and the purified condensate (144) are mixed to provide a combined product (166).

Fig.2

[0037] [Fig.2] shows a feedstock stream (202) containing a halide such as chlorine. This stream is optionally preheated, before being combined with a hydrogen rich gas stream (204) to a hydrogen enriched feedstock stream (206) in order to ensure the provision of the required hydrogen for the hydrogenation of di-olefins in first reactor (DOR). The hydrogen enriched feedstock stream (206) may optionally have been heated in one or both of a heat exchanger (shown) and other heating such as a fired heater (not shown) to provide sufficient temperature for activating the hydrogenation of di-olefins. The first reactor (DOR) is optional but may have operating conditions at a pressure of 30 Barg to 150 Barg and a temperature of about 180°C, suitable for hydrogenation of di-olefins. The first reactor (DOR) may contain a material catalytically active in olefin

saturation and hydro-dehalogenation. Within this first reactor (DOR), the hydrogen enriched hydrocarbon stream (206) would react in the presence of the catalytically active material, rendering a first hydrogenated product stream (208).

- [0038] The first hydrogenated product stream (208) is shown to be combined with an optional recycled hydrocarbon stream (210) which is heated, e.g. by heat exchange and the combined hydrogenated feed stream (212) is directed to a guard reactor (GRD) in which reactive heteroatoms react such that impurities are captured in a material catalytically active in hydrotreatment. The purified feedstock (214) is here heated further in a charge heater (CH) and directed to hydrotreatment in a hydrotreatment reactor (HDT) in which further heteroatoms such as nitrogen, sulfur, oxygen and halides are released as gaseous inorganic hydrogen compounds in a mixed gas/liquid stream of hydrotreated intermediate, which is cooled by heat exchange – here with the combined hydrogenated feed stream (212) and – in a boiler – with a stream of boiler feed water producing steam (220) for heating the hydrogen enriched feedstock stream (206).
- [0039] The mixed gas/liquid stream of hydrotreated intermediate (216) is directed to a hot high pressure stripper (HPST) operating at temperatures above the precipitation temperature for the concentration of ammonium halides in the mixed gas/liquid stream of hydrotreated intermediate (216). The stripping medium (221) is hydrogen which is also a consumed reagent in the upstream process. A stripped liquid product (222) and a stripper vapor (224) are withdrawn from the stripper. The stripper vapor (224) is combined with wash water (226) and the combined gas/water stream (228) is, after cooling, directed to a high pressure cold separator (HPCS), to separate the product in three phases; a recycle gas (230), which (optionally after further purification) is pressurized in recycle gas compressor (RCGC) and combined with make-up hydrogen gas (232) and directed as the hydrogen rich gas (204); sour water (234) which is directed to cleaning possibly involving separation of an amount of the water for reuse as wash water and finally a condensate product (236).
- [0040] The stripped liquid product (222) and the condensate product (236) are depressurized to a pressure from slightly above atmospheric pressure to 15 barg and directed to a fractionator stage, from which at least a bottom fraction (240) and a vapor fraction (242) are provided. To provide a stripping medium (238) for the fractionation, it is necessary to heat the heavy fraction, which typically would require a fired reboiler (FRB). An amount of liquid may also be recycled from this position.
- [0041] The vapor fraction (242) is combined with a stabilizer overhead stream (246) from a stabilizer (STAB) and an amount of wash water (248) and the combined water/stripper vapor stream (252) is after cooling directed to an overhead separator (OSEP) in which sour water (254) and fractionator overhead condensate (256) are condensed and separated from off-gas (258). The fractionator overhead condensate (256) is split

between an amount directed to stabilizer (STAB) and an amount directed as fractionator reflux (256) The stripped liquid hydrotreated intermediate (240) and the stabilized overhead condensate (262) to provide a combined product (266).

Description of Embodiments

- [0042] A first aspect of the present disclosure involves a process for conversion of a hydrocarbonaceous feed comprising at least 10 ppm_{wt}, 100 ppm_{wt} or 500 ppm_{wt} and less than 1000 ppm_{wt}, 5000 ppm_{wt} or 10000 ppm_{wt} of one or more halides, and at least 20 ppm_{wt}, 100 ppm_{wt} or 500 ppm_{wt} and less than 1000 ppm_{wt}, 5000 ppm_{wt} 10000 ppm_{wt} or 100000 ppm_{wt} organically bound nitrogen, to a hydrocarbon product stream by hydrotreatment, under effective hydrotreatment conditions, in the presence of a material catalytically active in hydrotreatment and an amount of hydrogen, wherein said conversion provides a mixed product stream comprises an amount of inorganic halides and an amount of ammonia, said process comprising the steps of separating in a first separation step at a first pressure and at a first separation temperature the mixed product stream to provide an overhead stream and a bottoms stream, combining the overhead stream with an amount of wash water and separating in a second separation step at a second pressure and at a second temperature the combined overhead stream and wash water in a non-polar stream of hydrocarbon condensate product, a polar stream of wash water comprising ammonium halides and a hydrogen rich gas phase stream, in a third separation step at a third pressure and at a third temperature, separating the bottoms stream in a liquid hydrocarbon and a first gas phase stream, in a fourth separation step at a fourth pressure and at a fourth temperature, separating the hydrocarbon condensate product in a purified hydrocarbon condensate and a second gas phase stream, characterized in that the first separation temperature being above the precipitation temperature with respect to ammonium halides in the mixed product stream, and the second pressure being at least 80% of said first pressure, the third pressure being below 50% of said first pressure and the fourth pressure being from 10% below to 10% above said third pressure.
- [0043] This has the associated benefit of enabling such a process with efficient separation without requiring fired heating in the separation process and while requiring little or no purification of the hydrocarbonaceous feedstock comprising halides and nitrogen, even if the hydrocarbonaceous feed is rich in halides and/or nitrogen such as a hydrocarbonaceous feed originating from thermal decomposition of plastic waste, municipal solid waste or sewage sludge.
- [0044] A second aspect involves a process according to the first aspect wherein one or both of the first gas phase stream and the second gas phase stream is combined with an amount of wash water as a combined overhead stream and in a fifth separation step at a

fifth pressure and a fifth temperature the combined overhead stream is separated in a gas phase stream, a non-polar stream of overhead condensate product and a polar stream of wash water comprising ammonium halides.

- [0045] This has the associated benefit of such a fifth separation step providing purification of the gas phase streams in the final purification step.
- [0046] A third aspect involves a process according to the first or second aspect wherein one or both of said third separation step and said fourth separation step are a stripping process employing a stripping medium.
- [0047] This has the associated benefit of enabling a process in which the separation is highly efficient, such that dissolved gases, including ammonia, halides, methane and carbon dioxide are driven out of the liquid separation product, by the stripping medium, which may be added gas or reboiled liquid.
- [0048] A fourth aspect involves a process according to the third aspect wherein said third separation step employs steam as a stripping medium.
- [0049] This has the associated benefit of enabling a process in which the liquid hydrocarbon is highly purified while said third separation step does not require reboiling by a fired heater, since the steam supports driving out impurities.
- [0050] A fifth aspect involves a process according to the third or fourth aspect wherein said fourth separation step is a reboiled stripping process, wherein heating for reboiling is provided by electrical heating, by heat exchange with steam or by heat exchange with a hot process stream, such as the liquid hydrocarbon stream from the third separation step.
- [0051] This has the associated benefit of enabling a process in which reboiling supports stripping off halides in the fourth separation step.
- [0052] A sixth aspect involves a process according to any aspect above, wherein the temperature of said first separation step is above 220°C, 250°C or 320°C and below 400°C.
- [0053] This choice of temperature has the benefit of being conveniently above the precipitation temperature of the ammonium halides, such that these are maintained in gas phase until combination with water.
- [0054] A seventh aspect involves a process according to any aspect above, wherein the temperature of said first separation step is below the temperature at which 5 wt%, 30 wt%, 50 wt%, 80 wt% or 95 wt% of the mixed product stream boils.
- [0055] This choice of temperature has the benefit of ensuring that an amount such as at least 95 wt%, 70 wt%, 50 wt%, 20 wt% or 5 wt% of the mixed product stream is withdrawn as a liquid from the first separator, to minimize the size of equipment in the overhead stream.
- [0056] An eighth aspect involves a process according to any aspect above, wherein the at

least an amount of the hydrocarbonaceous feed originates from a mixture rich in plastic, lignin, straw, lignocellulosic biomass, halide contaminated waste oils, aquatic biological material or sewage sludge.

- [0057] This has the associated benefit of such a process for conversion of a hydrocarbonaceous feed from such sources is environmentally benign and carried out in a safe and cost effective manner.
- [0058] A ninth aspect involves a process for conversion of a raw feed stream rich in molecules comprising C, H, N and one or more halides, and optionally O, S, Si, and other elements, said process comprising
- [0059] a step of thermal decomposition of said raw feed stream, to provide a precursor to a hydrocarbonaceous feed or a hydrocarbonaceous feed,
- [0060] optionally a step of pre-treatment, purifying the precursor to hydrocarbonaceous feed to provide the hydrocarbonaceous feed
- [0061] a hydrotreatment step for converting the hydrocarbonaceous feed in the presence of hydrogen, in accordance with any aspect above, to provide a hydrocarbon product stream.
- [0062] This has the associated benefit of such a process being able to receive a solid raw feed stream and converting it efficiently to a high quality hydrocarbon stream.
- [0063] A tenth aspect involves a process according to the eighth aspect above, wherein at least an amount of raw feed stream or the hydrocarbonaceous stream originates from a mixture rich in plastic, lignin, straw, lignocellulosic biomass, halide contaminated waste oils, aquatic biological material or sewage sludge.
- [0064] This has the associated benefit of such a process for production of a quality hydrocarbon product from such solid raw feed stream is environmentally benign and carried out in a safe and cost effective manner.
- [0065] An eleventh aspect involves a process according to any aspect above, followed by the step of directing the hydrocarbon product to a steam-cracking process.
- [0066] This has the associated benefit of providing a olefinic stream, e.g. for production of polymers.
- [0067] A twelfth aspect involves a system for hydrotreatment of a hydrocarbonaceous stream comprising a hydrotreatment reactor containing a material catalytically active in hydrotreatment, said hydrotreatment reactor comprising an inlet for introducing a hydrogen enriched hydrocarbon stream and an outlet for withdrawing a first hydrocarbon product stream, a first means of separation having at least an inlet, an overhead outlet and a bottoms outlet, a first means of mixing having two inlets and an outlet, a second means of separation, having an inlet and a liquid polar phase outlet, a liquid non-polar phase outlet and a gas phase outlet, a third means of separation having at least an inlet, an overhead outlet and a bottoms outlet, a fourth means of separation,

having an inlet, a liquid outlet and a gas phase outlet, wherein said outlet for withdrawing a first product stream is in fluid communication with the inlet of said first means of separation, wherein said overhead outlet is in fluid communication with the inlet of said first inlet of the first means of mixing, wherein a source of water is in fluid communication with the second inlet of the first means of mixing, wherein the outlet of the first means of mixing is in fluid communication with the inlet of the second means of separation, wherein the liquid outlet of the first means of separation is in fluid communication with the inlet of said third means of separation, wherein the liquid non-polar phase outlet of the second means of separation is in fluid communication with the inlet of said fourth means of separation, and wherein one or more of the liquid outlets of said third or fourth means of separation are individually or collectively in fluid connection with one or more product outlets.

- [0068] This has the associated benefit of providing a system for efficiently producing hydrocarbons from a hydrocarbonaceous material comprising nitrogen and halides.
- [0069] A thirteenth aspect involves a system according to the twelfth aspect above, where one or both of said third and fourth means of separation is a stripper further having a stripping medium inlet optionally being in fluid communication with a steam inlet or a reboiler in thermal communication with a hot process stream, steam or a further source of heat.
- [0070] This has the associated benefit of such a system with one or two strippers being able to provide a high purification of the product stream.
- [0071] A fourteenth aspect involves a system according to the thirteenth or twelfth aspect above, wherein one of the third means of separation and the fourth means of separation are positioned above the other, such as the third means of separation being positioned above the fourth means of separation.
- [0072] This has the associated benefit of such stacking of strippers enabling a process with a low footprint.
- [0073] A fifteenth aspect involves a system according to the fourteenth, thirteenth or twelfth aspect above further comprising a second means of mixing having two inlets and an outlet, a fifth means of separation, having an inlet and a liquid polar phase outlet, a liquid non-polar phase outlet and a gas phase outlet, wherein one or both of the gas phase outlets of said third and fourth means of separation are in fluid communication with the first inlet of the second means of mixing, wherein a source of water is in fluid communication with the second inlet of the second means of mixing, wherein the outlet of the second means of mixing is in fluid communication with the inlet of the fifth means of separation.

Examples

- [0074] The performance of two process layouts is compared in Table 1 and Table 2. In Example 1 a process layout according to [Fig.1] in which a hot separator provides a hot liquid stream and a cold condensate stream are directed independently for stripping is simulated. This is compared to Example 2 corresponding to [Fig.2], in which the product is stripped in a hot high pressure stripper, from which a purified product is directed to a fractionator and a hot contaminated gas stream is washed with water and separated in sour water, light gases and a condensate, and wherein the condensate is directed to the fractionator.
- [0075] The process of Example 1 involves simple – and imperfect - gas liquid separation and transfer of stream 122 with 30.1 t/h of the hot liquid stream at 295°C to further purification. Contrary to this the prior art process of Example 2 obtains early high quality purification by using a hot stripper receiving 0.7 t/h hydrogen at 99°C as stripping medium in stream 221, which cools the 27.2 t/h liquid stream 222 by 8°C to 287°C by and which increases the stripper vapor 224 outlet by the amounts of hydrogen stripping medium as well as dissolved naphtha and light hydrocarbon gases released from the hot liquid stream, which forms part of the hot separator high boiling liquid 122 of Example 1. This means more liquid hydrocarbons are condensed in the cold separator of Example 2, such that in Example 1 20.3 t/h at 50°C is transferred in stream 136 to purification vs. 23.1 t/h in stream 236 of Example 2. All in all, this has the consequence that less HCl but also less thermal energy is transferred to the final purification of Example 2 than of Example 1, and an amount of enthalpy is lost by combining the high boiling liquid and the condensate in the fractionator of Example 2. In addition, a higher amount of e.g. methane is also directed as recycle gas in stream 230, which requires a higher purge of recycle gas to minimize the impurities effect on the catalytic processes, and thus a higher amount of make-up hydrogen addition is also required.
- [0076] According to Example 1, the hot liquid phase may be stripped with steam in stream 138 having a temperature of 340°C, providing a stripping vapor outlet in stream 146 comprising 151 ppm_{wt} HCl at 295°C which is above the inorganic halide precipitation temperature. Furthermore, the heat of the hot liquid outlet 140 from the high temperature stripper has a temperature of 289°C and may be used to heat the amount stripped liquid 144 directed for reboiling of the low temperature stripper, to provide reboiled liquid as stripping medium.
- [0077] In comparison, in a scheme with fractionation of the combined streams such as Example 2, even though the fractionator vapor stream 242 contains only 2.5 ppm_{wt} HCl due to the higher removal of HCl at high pressure but in spite of the resulting lower inorganic halide precipitation temperature, the streams in to the fractionator will contain insufficient energy for releasing a fractionator vapor having a temperature

above the inorganic halide precipitation temperature, which is around 140°C.

Therefore, to ensure a vapor temperature above this limit in the process according to Example 2, energy is added – here by a fired reboiler, such that the temperature of the vapor stream 242 is at least 140°C to avoid precipitation prior to washing. This has the consequence that the cold overhead separator which will condense a sour water phase 254 and a liquid hydrocarbon condensate phase 256, but that the condensate 256 will comprise light gases, and thus must be directed to a stabilizer before being released as product.

[0078] The vapor output 224 from the high temperature stripper of Example 2 includes the hydrogen stripping medium, and thus the capacity of the recycle gas compressor of Example 2 must be larger than that of Example 1 since in Example 1, makeup hydrogen stream 132 may be added at discharge of the recycle gas compressor, and as a consequence increased amounts of wash water 226 will be required compared to the wash water 126 of Example 1. The reduced temperature of the amount of stripped liquid 222 directed for recycle in 210 also causes a requirement for larger heat exchangers in Example 2, and finally the process of Example 1 requires only 2 low pressure stripping columns, whereas the process of Example 2 requires a high pressure stripping column, a low pressure stripping column and a fractionator. Accordingly, the process layout of Example 1 has saving in investments as well as in operations.

[0079] The total cost of equipment of Example 1 will be 8-10% lower than in Example 2. The major savings will be (a) in replacing a high pressure stripper with a high pressure hot separator and a low pressure stripper, which approximately will be a 33% saving (b) reducing the cost of fired heaters by 50% by avoiding the fired reboiler and (c) reducing compressor capacity by 20%.

[0080] In addition the OPEX will be lower according to Example 1 due to 24% lower makeup gas addition and 16% lower recycle gas flow and the avoidance of fuel gas consumption for reboiler, corresponding to around 50% of the fuel gas consumption.

[Table 1]

		116	122	124	126	134	136	140	142	144	146	166
Temperature	[°C]	295	295	295	134	50	50	289	151	154	295	45
Flow	[t/h]	157.1	30.1	25.0	19.6	19.8	20.3	25.8	12.2	27.8	5.0	49.4

[Table 2]

		216	221	222	224	226	234	236	240	242	262	266
Temperature	[°C]	295	99	287	295	134	50	50	287	140	128	45
Flow	[t/h]	158.1	0.7	27.2	28.52	20.4	20.5	23.1	37.9	24.4	11.3	49.2

Claims

[Claim 1]

A process for conversion of a hydrocarbonaceous feed comprising at least 10 ppm_{wt} and less than 10000 ppm_{wt} of one or more halides, and at least 20 ppm_{wt} and less than 100000 ppm_{wt} organically bound nitrogen, to a hydrocarbon product stream by hydrotreatment, under effective hydrotreatment conditions, in the presence of a material catalytically active in hydrotreatment and an amount of hydrogen, wherein said conversion provides a mixed product stream comprises an amount of inorganic halides and an amount of ammonia, said process comprising the steps of

separating in a first separation step at a first pressure and at a first separation temperature the mixed product stream to provide an overhead stream and a bottoms stream,

combining the overhead stream with an amount of wash water and separating, in a second separation step at a second pressure and at a second temperature, the combined overhead stream and wash water into a non-polar stream of hydrocarbon condensate product, a polar stream of wash water comprising ammonium halides and a gas stream rich in hydrogen,

in a third separation step at a third pressure and at a third temperature, separating the bottoms stream in a liquid hydrocarbon and a first gas phase stream,

in a fourth separation step at a fourth pressure and at a fourth temperature, separating the hydrocarbon condensate product into a purified hydrocarbon condensate and a second gas phase stream,

characterized in that the first separation temperature being above the precipitation temperature with respect to ammonium halides in the mixed product stream,

and the second pressure being at least 80% of said first pressure, the third pressure being below 50% of said first pressure and and the fourth pressure being from 10% below to 10% above said third pressure.

[Claim 2]

A process according to claim 1 wherein said hydrocarbonaceous feed comprises at least 100 ppm_{wt} or 500 ppm_{wt} and less than 1000 ppm_{wt} or 5000 ppm_{wt} of one or more halides, and at least 100 ppm_{wt} or 500 ppm_{wt} and less than 1000 ppm_{wt}, 5000 ppm_{wt} or 10000 ppm_{wt} organically bound nitrogen.

- [Claim 3] A process according to claim 1 or 2 wherein one or both of the first gas phase stream and the second gas phase stream is combined with an amount of wash water as a combined overhead stream and in a fifth separation step at a fifth pressure and a fifth temperature the combined overhead stream is separated in a gas phase stream, a non-polar stream of overhead condensate product and a polar stream of wash water comprising ammonium halides.
- [Claim 4] A process according to claim 1, 2 or 3 wherein one or both of said third separation step and said fourth separation step are a stripping process employing a stripping medium.
- [Claim 5] A process according to claim 4 wherein said third separation step employs steam as a stripping medium.
- [Claim 6] A process according to claim 4 or 5 wherein said fourth separation step is a reboiled stripping process, wherein heating for reboiling is provided by electrical heating, by heat exchange with steam or by heat exchange with a hot process stream, such as the liquid hydrocarbon stream from the third separation step.
- [Claim 7] A process according to claim 1, 2, 3, 4, 5 or 6, wherein the temperature of said first separation step is above 220°C, 250°C or 320°C and below 400°C.
- [Claim 8] A process according to claim 1, 2, 3, 4, 5, 6 or 7 wherein the temperature of said first separation step is below the temperature at which 5 wt%, 30 wt%, 50 wt%, 80 wt% or 95 wt% of the mixed product stream boils.
- [Claim 9] A process according to claim 1, 2, 3, 4, 5, 6, 7 or 8, wherein at least an amount of the hydrocarbonaceous feed originates from a mixture rich in plastic, lignin, straw, lignocellulosic biomass, halide contaminated waste oils, aquatic biological material or sewage sludge.
- [Claim 10] A process for conversion of a raw feed stream rich in molecules comprising C, H, N and one or more halides, and optionally O, S, Si, and other elements, said process comprising
a step of thermal decomposition of said raw feed stream, to provide a precursor to a hydrocarbonaceous feed or a hydrocarbonaceous feed,
optionally a step of pre-treatment, purifying the precursor to hydrocarbonaceous feed to provide the hydrocarbonaceous feed
a hydrotreatment step for converting the hydrocarbonaceous feed in the presence of hydrogen, in accordance with any of the previous claims, to provide a hydrocarbon product stream.

- [Claim 11] A process according to claim 10, wherein the at least an amount of raw feed stream or the hydrocarbonaceous stream originates from a mixture rich in plastic, lignin, straw, lignocellulosic biomass, halide contaminated waste oils, aquatic biological material or sewage sludge.
- [Claim 12] A process according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11, followed by the step of directing the hydrocarbon product to a steam-cracking process.
- [Claim 13] A system for hydrotreatment of a hydrocarbonaceous stream comprising
a hydrotreatment reactor containing a material catalytically active in hydrotreatment, said hydrotreatment reactor comprising an inlet for introducing a hydrogen enriched hydrocarbon stream and an outlet for withdrawing a first hydrocarbon product stream,
a first means of separation having at least an inlet, an overhead outlet and a bottoms outlet,
a first means of mixing having two inlets and an outlet,
a second means of separation, having an inlet and a liquid polar phase outlet, a liquid non-polar phase outlet and a gas phase outlet,
a third means of separation having at least an inlet, an overhead outlet and a bottoms outlet,
a fourth means of separation, having an inlet, a liquid outlet and a gas phase outlet,
wherein said outlet for withdrawing a first product stream is in fluid communication with the inlet of said first means of separation,
wherein said overhead outlet is in fluid communication with the inlet of said first inlet of the first means of mixing,
wherein a source of water is in fluid communication with the second inlet of the first means of mixing,
wherein the outlet of the first means of mixing is in fluid communication with the inlet of the second means of separation,
wherein the liquid outlet of the first means of separation is in fluid communication with the inlet of said third means of separation,
wherein the liquid non-polar phase outlet of the second means of separation is in fluid communication with the inlet of said fourth means of separation,
and wherein one or more of the liquid outlets of said third or fourth means of separation are individually or collectively in fluid connection with one or more product outlets.

- [Claim 14] A system for hydrotreatment of a hydrocarbonaceous stream according to claim 13, where one or both of said third and fourth means of separation is a stripper further having a stripping medium inlet optionally being in fluid communication with a steam inlet or a reboiler in thermal communication with a hot process stream, steam or a further source of heat.
- [Claim 15] A system for hydrotreatment of a hydrocarbonaceous stream according to claim 13 or claim 14 wherein one of the third means of separation and the fourth means of separation are positioned above the other, such as the third means of separation being positioned above the fourth means of separation.