Title: PROCESS FOR DECHLORINATION OF HYDROCARBON STREAMS AND PYROLYSIS OILS

Abstract: A process for dechlorination of a hydrocarbon stream includes contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen to yield a hydrocarbon product which meets steam cracker requirements for chloride content, and in additional embodiments, requirements for olefin content.
PROCESS FOR DECHLORINATION OF HYDROCARBON STREAMS AND PYROLYSIS OILS

TECHNICAL FIELD

[0001] This disclosure relates the treatment of hydrocarbon streams via processes which include dechlorination.

BACKGROUND

[0002] Waste plastics contain polyvinylchloride (PVC). Through a pyrolysis process, waste plastics can be converted to gas and liquid products. These liquid products contain paraffins, i-paraffins (iso-paraffins), olefins, naphthenes, and aromatic components along with organic chlorides in concentrations of hundreds of ppm. However, the liquid products of a pyrolysis process (pyrolysis oils) are off-spec for use as a feedstock for steam crackers because steam cracker feed specifications require chloride levels less than 3 ppm and olefin content less than 1 wt%.

SUMMARY

[0003] A process for dechlorination of a hydrocarbon stream comprising contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen to yield a hydrocarbon product, wherein the hydrocarbon stream comprises one or more chloride compounds in a concentration of 5 ppm or more based on a total weight of the hydrocarbon stream, and recovering a treated hydrocarbon stream from the hydrocarbon product, wherein the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration of less than 5 ppm based on a total weight of the treated hydrocarbon stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Figure 1 illustrates a hydroprocessing system which dechlorinates chloride compounds, and in embodiments, additionally hydrogenates olefins contained in a hydrocarbon stream to levels suitable for introduction to a steam cracker.

[0005] Figure 2 is a graph of a staged catalyst sulphiding protocol, showing temperature versus time.

DETAILED DESCRIPTION

[0006] Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, and the like, used in the specification and claims are to be understood as modified in all instances by the term “about.” Various numerical ranges are disclosed herein. Because these ranges are continuous, they include every value between the minimum and maximum values. The endpoints of all ranges reciting the same characteristic or component are independently combinable and inclusive of the recited endpoint. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations. The endpoints of all ranges directed to the same component or property are inclusive of the endpoint and independently combinable.
The term "X or more" means that the named component is present in an amount of the value X, and values which are more than X.

[0007] The terms "a," "an," and "the" do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. As used herein the singular forms "a," "an," and "the" include plural referents.

[0008] As used herein, "combinations thereof" is inclusive of one or more of the recited elements, optionally together with a like element not recited, e.g., inclusive of a combination of one or more of the named components, optionally with one or more other components not specifically named that have essentially the same function. As used herein, the term "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0009] Reference throughout the specification to "an embodiment," "embodiments," "another embodiment," "other embodiments," "alternative embodiments," "additional embodiments," "some embodiments," and so forth (e.g., the use of "additionally" and/or "alternatively" in the context of describing one or more embodiments), means that a particular element (e.g., feature, structure, property, and/or characteristic) described in connection with the embodiment is included in at least an embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described element(s) can be combined in any suitable manner in the various embodiments.

[0010] Disclosed herein are embodiments of a process for dechlorination of a hydrocarbon stream which include contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen to yield a hydrocarbon product. Embodiments of the process include recovering a treated hydrocarbon stream from the hydrocarbon product, where the treated hydrocarbon stream has a reduced concentration of chloride compounds compared to the concentration of chloride compounds in the hydrocarbon feed stream.

[0011] Embodiments of the process are described in more detail with reference to Figure 1. Figure 1 illustrates a hydroprocessing system 100 which dechlorinates chloride compounds, and in embodiments, additionally hydrogenates olefins contained in a hydrocarbon stream 1 to levels suitable for introduction to a steam cracker 30. The system 100 includes a hydroprocessing reactor 10, a separator 20, and a steam cracker 30. The hydrocarbon stream 1 feeds to the hydroprocessing reactor 10, and the reaction product effluent flows from the hydroprocessing reactor 10 in the hydrocarbon product stream 2 to the separator 20. In separator 20, a treated product (e.g., in gas or liquid form) is recovered from the hydrocarbon product stream 2 and flows from the separator 20 via treated hydrocarbon stream 4, with one or more sulphur-containing gases and/or chlorine-containing gases flowing from the separator 20 in stream 3. Embodiments of the disclosure contemplate a second hydroprocessing reactor and a second separator may be placed in between separator 20 and treated hydrocarbon stream 4. The treated product flowing from the separator 20,
in such embodiments, may contain residual sulphur, and the second hydroprocessing reactor/second separator combination may treat the treated product flowing from the separator 20 to completely remove the sulphur such that a second treated product flowing in the treated hydrocarbon stream 4 from the second separator contains less than 200, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, 0.1 ppmw S based on total weight of the treated hydrocarbon stream 4.

[0012] The treated product in the treated hydrocarbon stream 4 may flow directly (e.g., without any separations or fractionations of the treated hydrocarbon stream 4) or via blended hydrocarbon stream 4’ (e.g., without any separations or fractionations of the treated hydrocarbon stream 4 and blended hydrocarbon stream 4’) to a steam cracker 30, from which high value products flow in stream 6.

[0013] The hydrocarbon stream 1 generally includes one or more hydrocarbons and one or more chloride compounds. In embodiments, the hydrocarbon stream 1 may additionally include one or more sulphides, hydrogen, or combinations thereof. The hydrocarbon stream 1 is generally in a liquid phase. A hydrogen (H₂) stream can be added to hydrocarbon stream 1 before entering the hydroprocessing reactor 10. Optionally, a H₂ stream is additionally added in between various catalyst beds in a multi-bed arrangement in the hydroprocessing reactor 10 to enrich the reactor environment with H₂.

[0014] The hydrocarbon stream 1 may be a stream from an upstream process, such as a pyrolysis process, which contains one or more chloride compounds, and optionally, also one or more sulphides, for example, from the pyrolysis of waste plastics. In an embodiment wherein the stream from the upstream process does not contain the one or more sulphides, the hydrocarbon stream 1 may be doped with the one or more sulphides, via a doping stream 7.

[0015] Examples of the one or more hydrocarbons which may be included in the hydrocarbon stream 1 include paraffins (n-paraffin, i-paraffin, or both), olefins, naphthenes, aromatic hydrocarbons, or combinations thereof. When the one or more hydrocarbons includes all the listed hydrocarbons, the group of hydrocarbons may be collectively referred to as a PONA feed (paraffin, olefin, naphthene, aromatics) or PIONA feed (n-paraffin, i-paraffin, olefin, naphthene, aromatics). A particular embodiment of the hydrocarbon stream 1 is a plastic pyrolysis oil, discussed in more detail below.

[0016] Any paraffin may be included in the hydrocarbon stream 1. Examples of paraffins which may be included in the hydrocarbon stream 1 include, but are not limited to, C₁ to C₂₂ n-paraffins and i-paraffins. In an embodiment, the concentration of paraffins in the hydrocarbon stream 1 may be less than 10 wt% based on the total weight of the hydrocarbon stream 1. Alternatively, the concentration of paraffins in the hydrocarbon stream 1 may be 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, or more based on the total weight of the hydrocarbon stream 1. While embodiments include paraffins of carbon numbers up to 22, the disclosure is not limited to carbon number 22 as an upper end-point of the suitable range of paraffins,
and the paraffins can include higher carbon numbers, e.g., 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, and higher.

[0017] Any olefin may be included in the hydrocarbon stream 1. Examples of olefins which may be included in hydrocarbon stream 1 include, but are not limited to, C2 to C10 olefins and combinations thereof. In an embodiment, the concentration of olefins in the hydrocarbon stream 1 may be less than 10 wt% based on the total weight of the hydrocarbon stream 1. Alternatively, the concentration of olefins in the hydrocarbon stream 1 may be 10 wt%, 20 wt%, 30 wt%, 40 wt% or more based on the total weight of the hydrocarbon stream 1. While embodiments include olefins of carbon numbers up to 10, the disclosure is not limited to carbon number 10 as an upper end-point of the suitable range of olefins, and the olefins can include higher carbon numbers, e.g., 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, and higher.

[0018] In an embodiment, the hydrocarbon stream 1 comprises no olefins.

[0019] Any naphthene may be included in the hydrocarbon stream 1. Examples of naphthenes include, but are not limited to, cyclopentane, cyclohexane, cycloheptane, and cyclooctane. In an embodiment, the concentration of naphthenes in the hydrocarbon stream 1 may be less than 10 wt% based on the total weight of the hydrocarbon stream 1. Alternatively, the concentration of naphthenes in the hydrocarbon stream 1 may be 10 wt%, 20 wt%, 30 wt%, 40 wt% or more based on the total weight of the hydrocarbon stream 1. While embodiments include naphthenes of carbon numbers up to 8, the disclosure is not limited to carbon number 8 as an upper end-point of the suitable range of naphthenes, and the naphthenes can include higher carbon numbers, e.g., 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, and higher.

[0020] Any aromatic hydrocarbon may be included in the hydrocarbon stream 1. Aromatic hydrocarbons suitable for use in the hydrocarbon stream 1 include, but are not limited to, benzene, toluene, xylenes, ethyl benzene, or combinations thereof. In an embodiment, the concentration of aromatic hydrocarbons in the hydrocarbon stream 1 may be less than 10 wt% based on the total weight of the hydrocarbon stream 1. Alternatively, the concentration of aromatic hydrocarbons in the hydrocarbon stream 1 may be 10 wt%, 20 wt%, 30 wt%, 40 wt% or more based on the total weight of the hydrocarbon stream 1. While embodiments include aromatic hydrocarbons of carbon numbers up to 8, the disclosure is not limited to carbon number 8 as an upper end-point of the suitable range of aromatic hydrocarbons, and the aromatic hydrocarbons can include higher carbon numbers, e.g., 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, and higher. In an embodiment, the aromatic hydrocarbons carbon number is as high as 22.

[0021] In an embodiment, the hydrocarbon stream 1 comprises no aromatic hydrocarbons.
Chloride compounds which may be included in the hydrocarbon stream 1 include, but are not limited to, aliphatic chlorine-containing hydrocarbons, aromatic chlorine-containing hydrocarbons, and other chlorine-containing hydrocarbons. Examples of chlorine-containing hydrocarbons include, but are not limited to, 1-chlorohexane (C₆H₁₃Cl), 2-chloropentane (C₅H₁₁Cl), 3-chloro-3-methyl pentane (C₇H₁₅Cl), (2-chloroethyl) benzene (C₉H₁₀Cl), chlorobenzene (C₈H₇Cl), or combinations thereof. The concentration of chloride compounds in the hydrocarbon stream 1 may be 5 ppm, 6 ppm, 7 ppm, 8 ppm, 9 ppm, 10 ppm, 15 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm, 700 ppm, 800 ppm, 900 ppm, 1,000 ppm, 1,100 ppm, 1,200 ppm, 1,300 ppm, 1,400 ppm, 1,500 ppm, 1,600 ppm, 1,700 ppm, 1,800 ppm, 1,900 ppm, 2,000 ppm or more based on the total weight of the hydrocarbon stream 1.

Sulphides which may be included in the hydrocarbon stream 1 include sulphur-containing compounds. For example, a sulphiding agent such as dimethyl disulphide (C₇H₁₆S₂), dimethyl sulphide (C₅H₁₂S), mercaptans (R-SH), carbon disulphide (CS₂), hydrogen sulphide (H₂S), or combinations thereof may be used as the sulphide in the hydrocarbon stream 1.

In an embodiment, one or more sulphides (e.g., dimethyl disulphide (C₇H₁₆S₂), dimethyl sulphide (C₅H₁₂S), mercaptans (R-SH), carbon disulphide (CS₂), hydrogen sulphide (H₂S), or combinations thereof) are added to the hydrocarbon stream 1 (e.g., the hydrocarbon stream 1 is "doped" with one or more sulphides), for example, via a doping stream 7, before the hydrocarbon stream 1 is introduced to the hydroprocessing reactor 10. In such embodiments, the one or more sulphides are added to the hydrocarbon stream 1 in an amount such that a sulphur content of the hydrocarbon stream 1, after sulphide addition, is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, 5 wt% or more based on the total weight of the hydrocarbon stream 1. In embodiments, the doping stream 7 may include components tailored for doping such as hexadecane and dimethyl disulphide; alternatively, the doping stream 7 may be a heavier oil (e.g., naphtha, diesel, or both) which already contains sulphide compounds (or to which sulphides are doped to achieve the sulphur content disclosed herein) and which is blended with the hydrocarbon stream 1 to achieve the sulphur content described above.

In alternative embodiments, one or more sulphides are present in the hydrocarbon stream as a result of upstream processing from which the hydrocarbon stream 1 flows. In such embodiments, the hydrocarbon stream 1 may contain one or more sulphides in an amount such that a sulphur content of the hydrocarbon stream 1, without sulphide doping, is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, 5 wt% or more based on the total weight of the hydrocarbon stream 1.

In yet other embodiments, the hydrocarbon stream 1 may contain one or more sulphides in an amount insufficient for sulphiding (e.g., less than 5,000, 4,000, 3,000, 2,000, 1,000, 900, 800, 700, 600, 500, 400, 300, 200, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 5, or 1 ppm) the hydroprocessing catalyst contained in
the hydroprocessing reactor 10 (the catalyst is discussed in more detail below), and doping stream 7 is utilized to raise the concentration of the one or more sulphides in the hydrocarbon stream 1 to such that a sulphur content of the hydrocarbon stream 1, after sulphide addition, is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, 5 wt% or more based on the total weight of the hydrocarbon stream 1.

[0027] In an embodiment, the sulphur content of the hydrocarbon stream 1, after sulphide addition using doping stream 7, is up to about 3 wt% based on the total weight of the hydrocarbon stream 1. In another embodiment, the sulphur content of the hydrocarbon stream 1, without sulphide addition using doping stream 7, is up to about 3 wt% based on the total weight of the hydrocarbon stream 1.

[0028] In embodiments, the hydrocarbon stream 1 may be one or more plastic pyrolysis oils which contain any of the paraffins, i-paraffins, olefins, naphthenes, aromatic hydrocarbons, chloride compounds, sulphides, or combinations thereof as disclosed herein. The one or more plastic pyrolysis oils may be obtained from pyrolysis of waste plastics (for example, from a high severity process as disclosed in U.S. Patent No. 8,895,790, which is incorporated by reference in its entirety, or from any low temperature severity pyrolysis process known in the art with the aid of this disclosure).

[0029] Other streams which may comprise at least a portion of the hydrocarbon stream 1 include a reformate stream from catalytic naphtha reformer, tire pyrolysis oil, and any other chloride containing hydrocarbon stream.

[0030] In embodiments, the hydrocarbon stream 1 may be one or more pyrolysis oils as described above which is blended with a heavier oil (e.g., a naphtha or diesel, via doping stream 7). In such embodiments, blending the treated hydrocarbon stream 4 with a non-chlorinated stream 5 as described for embodiments below may additionally occur; alternatively, the subsequent blending may not occur.

[0031] The hydroprocessing reactor 10 is configured to dechlorinate, and in some embodiments, additionally hydrogenate components of the hydrocarbon stream 1 fed to the hydroprocessing reactor 10. In the hydroprocessing reactor 10, the hydrocarbon stream 1 is contacted with the hydroprocessing catalyst in the presence of hydrogen to yield a hydrocarbon product in stream 2. It is contemplated the hydrocarbon stream 1 may be contacted with the hydroprocessing catalyst in upward flow, downward flow, radial flow, or combinations thereof, with or without a staged addition of hydrocarbon stream 1, doping stream 7, a H₂ stream, or combinations thereof. It is further contemplated the components of the hydrocarbon stream 1 may be in the liquid phase, a liquid-vapor phase, or a vapor phase while in the hydroprocessing reactor 10.

[0032] The hydroprocessing reactor 10 may facilitate any reaction of the components of the hydrocarbon stream 1 in the presence of, or with, hydrogen. Reactions may occur as the addition of hydrogen atoms to double bonds of unsaturated molecules (e.g., olefins, aromatic compounds), resulting in saturated molecules (e.g., paraffins, i-paraffins, naphthenes). Additionally or alternatively, reactions in the
hydroprocessing reactor 10 may cause a rupture of a bond of an organic compound, with a subsequent reaction and/or replacement of a heteroatom with hydrogen. Examples of reactions which may occur in the hydroprocessing reactor 10 include, but are not limited to, the hydrogenation of olefins, removal of heteroatoms from heteroatom-containing hydrocarbons (e.g., dechlorination), conversion of one or more aromatics to one or more cycloparaffins, isomerization of one or more normal paraffins to one or more i-paraffins, selective ring opening of one or more cycloparaffins to one or more i-paraffins, or combinations thereof.

In embodiments, the hydroprocessing reactor 10 may be any vessel configured to contain the hydroprocessing catalyst disclosed herein. The vessel may be configured for gas phase, liquid phase, vapor-liquid phase, or slurry phase operation. The hydroprocessing reactor 10 may include one or more beds of the hydroprocessing catalyst in fixed bed, fluidized bed, moving bed, ebullated bed, slurry bed, or combinations thereof, configuration. The hydroprocessing reactor 10 may be operated adiabatically, isothermally, nonadiabatically, non-isothermally, or combinations thereof. The reactions of this disclosure may be carried out in a single stage or in multiple stages. For example, the hydroprocessing reactor 10 can be two reactor vessels fluidly connected in series, each having one or more catalyst beds of the hydroprocessing catalyst. Alternatively, two or more stages for hydroprocessing may be contained in a single reactor vessel. In embodiments having multiple stages, the first stage may dechlorinate and hydrogenate components of the hydrocarbon stream 1 to yield a first hydrocarbon product having a first level of chloride compounds and olefins. The first hydrocarbon product may flow from the first stage to the second stage, where other components of the first hydrocarbon product are dechlorinated and hydrogenated to yield a second hydrocarbon product stream (stream 2 in Figure 1) having a second level of chloride compounds and olefins. The second hydrocarbon product stream may then be treated as described herein for stream 2.

In an embodiment, the hydroprocessing reactor 10 may comprise one or more vessels.

In embodiments of a single vessel or multiple vessels, the sulphur present in the hydrocarbon stream 1 is removed as H₂S to provide a reduced level of sulphur acceptable for downstream processing in steam crackers and refinery units.

In an embodiment, hydrogen may feed to the hydroprocessing reactor 10 in stream 8. The rate of hydrogen addition to the hydroprocessing reactor 10 is generally sufficient to achieve the hydrogen-to-hydrocarbon ratios disclosed herein.

The disclosed hydroprocessing reactor 10 may operate at various process conditions. For example, contacting the hydrocarbon stream 1 with the hydroprocessing catalyst in the presence of hydrogen may occur in the hydroprocessing reactor 10 at a temperature of 100 °C to 450 °C; alternatively, 100 °C to 350 °C; or alternatively, 260 °C to 350 °C. Contacting the hydrocarbon stream 1 with the
hydroprocessing catalyst in the presence of hydrogen may occur in the hydroprocessing reactor 10 at a pressure of 1 bar to 200 bar; or alternatively, 20 bar to 60 bar. Contacting the hydrocarbon stream 1 with the hydroprocessing catalyst in the presence of hydrogen may occur in the hydroprocessing reactor 10 at a weight hourly space velocity (WHSV) of between 0.1 hr⁻¹ to 10 hr⁻¹; or alternatively, 1 hr⁻¹ to 3 hr⁻¹. Contacting the hydrocarbon stream 1 with the hydroprocessing catalyst in the presence of hydrogen may occur in the hydroprocessing reactor 10 at a hydrogen-to-hydrocarbon (H₂/HC) flow ratio of 10 to 3,000 NL/L; or alternatively, 200 to 800 NL/L.

[0038] It is contemplated that dechlorination using the hydroprocessing catalyst as described herein is performed in the hydroprocessing reactor 10 without the use of chlorine sorbents, without addition of Na₂CO₃ in an effective amount to function as a dechlorinating agent, or both.

[0039] The hydroprocessing catalyst may be any catalyst used for hydrogenation (e.g., saturation) of olefins and aromatic hydrocarbons (e.g., a commercially available hydrotreating catalyst). In an embodiment, the hydroprocessing catalyst is a cobalt and molybdenum catalyst (Co-Mo catalyst) on an alumina support. In other embodiments, the hydroprocessing catalyst is a nickel and molybdenum catalyst (Ni-Mo catalyst) on an alumina support or tungsten and molybdenum catalyst (W-Mo catalyst) on an alumina support. Other catalyst embodiments may include platinum and palladium catalyst (Pt-Pd catalyst) on an alumina support, nickel sulphides suitable for slurry processing, molybdenum sulphides suitable for slurry processing, nickel and molybdenum sulphides, or combinations thereof.

[0040] In embodiments, the hydroprocessing catalyst is activated and/or the activity is maintained by sulphiding the hydroprocessing catalyst. For example, the hydroprocessing catalyst may be sulphided (i.e., activated) and/or sulphiding (i.e., maintaining of the catalyst activity) of the hydroprocessing catalyst may be performed (e.g., maintaining the hydroprocessing catalyst in sulphided form is accomplished) by continuously contacting the hydrocarbon stream 1 containing one or more sulphides with the hydroprocessing catalyst. The one or more sulphides may be included in the hydrocarbon stream 1 in an amount such that the sulphur content of the hydrocarbon stream 1 is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, or 5 wt% based on the total weight of the hydrocarbon stream 1. In an embodiment, the sulphur content of the hydrocarbon stream 1 is up to about 3 wt% based on the total weight of the hydrocarbon stream 1.

[0041] Alternatively, the hydroprocessing catalyst may be sulphided (i.e., activated) by contacting a catalyst activating stream 9 containing one or more sulphides with the hydroprocessing catalyst for a period of time (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9 or more hours) sufficient to activate the hydroprocessing catalyst (before contacting the hydrocarbon stream 1 with the hydroprocessing catalyst). In such embodiments, the catalyst activating stream 9 may include a hydrocarbon carrier for the one or more sulphides, such as hexadecane. The one or more sulphides may be included in the catalyst activating stream 9 in an amount such that the
sulphur content of the catalyst activating stream 9 is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, 5 wt% or more based on the total weight of the catalyst activating stream 9. In an embodiment, the sulphur content of the catalyst activating stream 9 is up to about 3 wt% based on the total weight of the catalyst activating stream 9. After the hydroprocessing catalyst is activated with the catalyst activating stream 9, flow of the catalyst activating stream 9 may be discontinued, and sulphiding (i.e., maintaining catalyst activity) of the hydroprocessing catalyst may be maintained (e.g., maintaining the hydroprocessing catalyst in sulphided form is accomplished) by continuously contacting the hydrocarbon stream 1 containing one or more sulphides with the hydroprocessing catalyst. The one or more sulphides may be included in the hydrocarbon stream 1 in an amount such that the sulphur content of the hydrocarbon stream 1 is about 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, or 5 wt% based on the total weight of the hydrocarbon stream 1. In an embodiment, the sulphur content of the hydrocarbon stream 1 is up to about 3 wt% based on the total weight of the hydrocarbon stream 1.

[0042] In embodiments, catalyst activity is also maintained by chloriding the hydroprocessing catalyst. The hydroprocessing catalyst is chlorided using the one or more chloride compounds provided to the hydroprocessing catalyst by the hydrocarbon stream 1. The one or more chloride compounds which contribute to acidification of the hydroprocessing catalyst may be included in the hydrocarbon stream 1 in concentrations disclosed herein.

[0043] Due to hydrogenation reactions in the hydroprocessing reactor 10, in embodiments, the hydrocarbon product stream 2 may contain one or more olefins in a concentration of less than 1 wt% based on the total weight of the hydrocarbon product stream 2. It is also contemplated that the concentration of aromatic hydrocarbons in the hydrocarbon product stream 2 is less than the concentration of aromatic hydrocarbons in the hydrocarbon stream 1 due to hydrogenation of at least a portion of the aromatic hydrocarbons in the hydroprocessing reactor 10. For example, aromatic hydrocarbons may be present in the hydrocarbon product stream 2 in a concentration of less than 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 wt% based on the total weight of the hydrocarbon product stream 2.

[0044] The reaction product flows as effluent from the hydroprocessing reactor 10 in the hydrocarbon product stream 2 to the separator 20. Separator 20 may be any vessel which can recover a treated hydrocarbon stream 4 from the hydrocarbon product 2 which is fed to the separator 20. In embodiments, the treated hydrocarbon stream 4 may be recovered by separating a treated product (e.g., liquid product or gas product) from sulphur and chlorine-containing gas in the separator 20, and by flowing the treated product in the treated hydrocarbon stream 4 from the separator 20.

[0045] In an embodiment, the separator 20 is a condenser which operates at conditions which condense a portion of the hydrocarbon product stream 2 into the treated product (e.g., liquid product or treated liquid product) while leaving sulphur and chlorine-containing compounds in the gas phase. The treated liquid
product flows from the separator 20 in treated hydrocarbon stream 4, and the sulphur and chlorine-containing gas flows from the separator 20 via stream 3.

[0046] In another embodiment, the separator 20 is a scrubbing unit containing a caustic solution (e.g., a solution of sodium hydroxide in water) which removes (e.g., via reaction, adsorption, absorption, or combinations thereof) sulphur and chlorine-containing gases from the hydrocarbon product stream 2 to yield the treated product (e.g., gas product or treated gas product) which flows from the separator 20 via treated hydrocarbon stream 4 while the sulphur and chlorine-containing compounds in the gas phase flow from the separator 20 via stream 3.

[0047] In yet another embodiment, the separator 20 is a condenser in communication with a scrubbing unit containing a caustic solution. As described above, the condenser may operate at conditions which condense a portion of the hydrocarbon product stream 2 into the mid-treated product (e.g., liquid product or treated liquid product) while leaving sulphur and chlorine-containing compounds in the gas phase. The mid-treated liquid product flows from the condenser and experiences a pressure reduction (e.g., via a valve or other pressure reducing device known in the art with the aid of this disclosure) which creates an effluent gas which flows from the scrubbing unit, leaving the treated product flowing in treated hydrocarbon stream 4. Sulphur and chlorine-containing compounds flow from the separator 20 in stream 3.

[0048] In embodiments disclosed herein, no hydrogen halides and no halogenated organic compounds are recycled to the hydroprocessing reactor 10.

[0049] In embodiments, the treated hydrocarbon stream 4 includes one or more chloride compounds in a concentration of less than 5 ppm, 4 ppm, 3 ppm, 2 ppm, 1 ppm, or 0.5 ppm based on a total weight of the treated hydrocarbon stream 4. It is contemplated that the one or more chloride compounds in the treated hydrocarbon stream 4 may be the same as some or all of the one or more chloride compounds in the hydrocarbon stream 1; alternatively, it is contemplated that only some of the one or more chloride compounds in the treated hydrocarbon stream 4 are the same as only some of the one or more chloride compounds in the hydrocarbon stream 1; alternatively, it is contemplated that none of the one or more chloride compounds in the treated hydrocarbon stream 4 are the same as the one or more chloride compounds in the hydrocarbon stream 1.

[0050] In additional embodiments, the treated hydrocarbon stream 4 includes the one or more olefins in a concentration which is less than a concentration of the one or more olefins in the hydrocarbon stream 1 due to hydrogenation of at least a portion of the one or more olefins from the hydrocarbon stream 1 while the hydrocarbon stream 1 is contacted with the hydroprocessing catalyst in the hydroprocessing reactor 10. In an embodiment, the one or more olefins are present in the treated hydrocarbon stream 4 in a concentration of less than 1 wt% based on the total weight of the treated hydrocarbon stream 4.
[0051] In embodiments, the treated hydrocarbon stream 4 includes one or more paraffins, and the concentration of the one or more olefins is less than 1 wt% based on the total weight of the treated hydrocarbon stream 4.

[0052] In embodiments where the treated hydrocarbon stream 4 includes one or more chloride compounds in a concentration of less than 3 ppm, the treated hydrocarbon stream 4 may be fed directly to the steam cracker 30. In alternative embodiments where the treated hydrocarbon stream 4 includes one or more chloride compounds in a concentration of 3 ppm or more (e.g., 3 ppm to 5 ppm), the treated hydrocarbon stream 4 may be blended with a non-chlorinated hydrocarbon stream 5 to yield a blended hydrocarbon stream 4' (streams 4' and 5 having dashed lines to denote the alternative embodiment) having a concentration of one or more chlorides which is less than 3 ppm based on a total weight of the blended hydrocarbon stream 4'. The blended hydrocarbon stream 4' may be fed to the steam cracker 30.

[0053] Steam cracker 30 generally has feed specification requirements. First, the steam cracker 30 requires the concentration of chloride compounds in the feed to the steam cracker 30 to be less than 3 ppm. Second, the steam cracker 30 requires the concentration of olefins in a stream fed to the steam cracker 30 to be less than 1 wt%. The steam cracker 30 cracks molecules or cleaves at elevated temperatures carbon-carbon bonds of the components in the treated hydrocarbon stream 4 or blended hydrocarbon stream 4' in the presence of steam to yield high value products such as ethylene, propylene, butene, butadiene, aromatic compounds, or combinations thereof. The high value products may flow from the steam cracker 30 via stream 6.

[0054] As is demonstrated in the examples below, it has been found that dechlorination according to the embodiments disclosed herein can occur over the operating temperature ranges disclosed herein for the hydroprocessing reactor 10, including operating temperatures in the low-end of the temperature ranges disclosed herein. Removal of chloride compounds to less than 1 ppm occurs at temperatures below 350 °C. Moreover, achieving sub-ppm chloride compound concentrations is possible with initial chloride content in the hydrocarbon stream 1 of 1,000 ppm or more. Moreover still, removal of chloride compounds is effective for different types and classes of chlorides present in the hydrocarbon stream 1. When the hydروprocessing reaction is conducted at temperatures at or above 350 °C, it has been found that the treated hydrocarbon product contains 3ppm or higher chloride content. In such cases, the treated hydrocarbon product stream can be blended as described herein with a non-chlorinated stream 5 in such proportions to make the combined blended hydrocarbon stream 4' meet the steam cracker feed specifications.

[0055] Operation at low temperatures (e.g., less than 350 °C) also has an added advantage of corrosion mitigation of the reactor metallurgy. For most metals and alloys used in the commercial reactors, corrosion rates start to increase at reactor temperatures over 300 °C. It has been found that the efficiency of dechlorination according to the disclosed embodiments is good at reactor temperatures below 350 °C, and
the dechlorination process works with a sulphided Co-Mo catalyst on an alumina support even as low as 260 °C, with the chlorides in the treated product being less than 1 ppm. Thus, the metallurgy corrosion issue is mitigated and longer equipment life is possible while achieving dechlorination to levels desirable for feed to steam cracker 30. The processes disclosed herein have been demonstrated to work at pressures as low as 20 barg, which is a less severe condition than the conditions typically employed with a commercial hydrotreating catalyst. Ability to operate at lower pressures reduces the required pressure rating for process vessels (e.g., the hydroprocessing reactor 10) and provides an opportunity for reduced investment costs.

[0056] The disclosed embodiments also demonstrate olefins in the hydrocarbon product are reduced typically to less than 1 wt% of the treated hydrocarbon stream 4 from a feed olefin concentration of 20 wt% or more in the hydrocarbon stream 1. Thus, the disclosed processes achieve the requirements of chloride content and olefin content of the feed for a steam cracker 30.

EXAMPLES

[0057] The subject matter having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification of the claims to follow in any manner.

[0058] Examples 1 to 5 were conducted in a fixed bed reactor located inside a 3-zone split-tube furnace. The reactor internal diameter was 13.8 mm and had concentrically located bed thermowell of 3 mm outer diameter. The reactor was 48.6 cm long. Commercial hydroprocessing catalyst of Co-Mo on alumina (8 g bone dry weight) was broken along the length to particles of 1.5 mm long and diluted with SiC in the ratio of 60 % SiC to 40 % catalyst to give a mean particle diameter of 0.34 mm. This was done to avoid slip through of the chlorides due to wall slip or channeling in the small diameter reactor. Pre-heating bed and post-catalyst inert beds was provided in the form of 1 mm glass beads. The catalyst bed temperature was controlled to isothermal by varying the controlled furnace zone skin temperatures. The hydroprocessing catalyst was sulphided using 3 wt% S in hexadecane (S was introduced as dimethyl disulphide). Liquid feed (i.e., the hydrocarbon stream) was fed through a metering pump and H₂ gas was fed using a mass flow controller. The reactor effluent gases (i.e., hydrocarbon product) were cooled to condense out the liquids (i.e., the treated hydrocarbon stream in the form of a liquid product) under pressure while allowing non-condensed gases (e.g., containing chloride(s), chlorine, hydrogen sulphide, or combinations thereof) to separate. Following liquid condensation, the pressure of the liquids was reduced and effluent gas flow was scrubbed in a caustic scrubber and measured using a drum-type wet gas meter. The effluent gas flow was analyzed using a refinery gas analyzer (a custom gas analyzer from M/s AC Analyticals BV). The liquid product olefin content was determined using a Detailed Hydrocarbon Analyzer GC (DHA), and a boiling point characterization was obtained using a SIMDIS GC. The liquid
product chloride content was measured using a Chlora M-series analyzer (monochromatic wavelength dispersive X-ray Fluorescence technique, ASTM D7536).

EXAMPLE 1

[0059] In Example 1, a feed was prepared by mixing plastic pyrolysis oil (36.3 g) with n-hexadecane (240 g), and then adding dimethyl disulphide (the sulphide) and 1-chlorohexane (the chloride compound) to give a sulphur content of 2.34 wt% and 836 ppm chloride in the feed. This feed was used as a hydrocarbon stream which was contacted with the sulphided hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H₂ under several operating conditions as provided in the table below:

<table>
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<th>T, °C</th>
<th>P, barg</th>
<th>WHSV, hr⁻¹</th>
<th>H₂/HC, NL/L</th>
<th>Cl, ppm in liquid product</th>
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[0060] Example 1 demonstrates it is possible to dechlorinate a hydrocarbon stream containing plastic pyrolysis oil and having chloride compounds from a chloride content of more than 800 ppm chlorides to less than 5 ppm in the liquid product. As can be seen from the above table, the chloride content of the liquid product (i.e., the treated hydrocarbon stream) increases when the reactor bed temperature is increased to at or above 350 °C. At temperatures below 350 °C, Example 1 demonstrates removal of chloride compounds to chloride contents less than 3 ppm, and even sub-ppm levels.

EXAMPLE 2

[0061] In Example 2, a feed was prepared by adding dimethyl disulphide (the sulphide) and 2-chloropentane, 3-chloro-3-methyl pentane, 1-chlorohexane, (2-chloroethyl) benzene, and chlorobenzene (the chloride compounds) to n-hexadecane to give a sulphur content of 2wt% in the mixture and a chloride content of 1,095 ppm in the mixture. Each of the chloride compounds contributed approximately 220 ppm to the feed mixture. This feed was used as a hydrocarbon stream which was contacted with the hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H₂ at 300 °C reactor bed temperature, 40 barg reactor pressure, 414 NL/L H₂/HC flow ratio, and 0.92 hr⁻¹ weight hourly space velocity (WHSV). The chloride content of the liquid product (i.e., treated hydrocarbon stream) was 0.23 ppm.

[0062] Example 2 demonstrates it is possible to dechlorinate a hydrocarbon stream containing no olefins and chloride compounds from a chloride content of about 1,100 ppm chlorides to the sub-ppm level in the in the liquid product.
EXAMPLE 3

[0063] In Example 3, a hydrocarbon feed mixture was prepared to contain 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. To this the organic chlorides mentioned in Example 2 above were added along with dimethyl disulphide to give 205 ppm organic chlorides and 2 wt% S in the mixture. This feed was used as a hydrocarbon stream which was contacted with the hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H₂ at conditions of 300 °C reactor temperature, 60 barg reactor pressure, 0.92 hr⁻¹ WHSV and 414 NL/L H₂/HC flow ratio. The liquid product (analyzed in DHA) contained 0.183 wt% olefins and 0.11 ppmw chlorides.

[0064] Example 3 demonstrates removal of olefins from a hydrocarbon stream such that the liquid product has less than 1 wt% olefin content needed in a steam cracker feed.

EXAMPLE 4

[0065] In Example 4, a hydrocarbon feed mixture was prepared to contain 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. To this the organic chlorides mentioned in Example 2 above were added along with dimethyl disulphide to give 205 ppm organic chlorides and 2 wt% S in the mixture. This feed was used as a hydrocarbon stream which was contacted with the hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H₂ at conditions of 260 °C reactor temperature, 60 barg reactor pressure, 0.92 hr⁻¹ WHSV and 414 NL/L H₂/HC flow ratio. The liquid product (i.e., the treated hydrocarbon stream) contained 0.1 ppm chloride.

[0066] Example 4 demonstrates the effective removal of chloride compounds from a hydrocarbon stream at very low temperatures.

EXAMPLE 5

[0067] In Example 5, a hydrocarbon feed mixture was prepared to contain 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. To this the organic chlorides mentioned in Example 2 above were added along with dimethyl disulphide to give 205 ppm organic chlorides and 2 wt% S in the mixture. This feed was used as a hydrocarbon stream which was contacted with the hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H₂ at conditions of 300 °C reactor temperature, 20 barg reactor pressure, 0.92 hr⁻¹ WHSV and 414 NL/L H₂/HC flow ratio. The liquid product (i.e., the treated hydrocarbon stream) contained 0.09 ppmw chloride and 0.05 wt% olefins.

[0068] Example 5 demonstrates the effective removal of chloride compounds from a hydrocarbon stream at low operating pressures.
EXAMPLE 6

[0069] Example 6 demonstrates a process for sulphiding a hydroprocessing catalyst. The particular steps of the process are shown in Figure 2. The time of 0 hours (zero time) in Figure 2 corresponds to a time after the hydroprocessing catalyst is introduced into the hydroprocessing reactor.

[0070] At ambient temperature, the hydroprocessing reactor (having previously been loaded with the hydroprocessing catalyst) was purged with hydrogen for 30 to 60 minutes at a set operating pressure (e.g., 40 to 60 barg). The set operating pressure was maintained by venting the reactor when the pressure of the reactor during hydrogen purging increased above the set operating pressure (e.g., due to a hydrogen source pressure greater than the set operating pressure).

[0071] After purging the hydroprocessing reactor for 30-60 minutes at ambient temperature, the hydrogen purge was stopped.

[0072] Still at the ambient temperature, the sulphiding feed was then introduced into the reactor using a high pressure pump against the set reactor pressure at a weight hourly space velocity (WHSV) of 3 hr⁻¹ (on bone-dry catalyst basis). The sulphiding feed (e.g., for use in doping stream 7 of Figure 1) was prepared by mixing n-hexadecane with dimethyl disulphide in appropriate quantity to give 3 wt% sulphur based on total weight of the sulphiding feed. For the sulphiding feed, as per catalyst sulphiding protocol followed, cracked feedstock cannot be used. Hence, n-hexadecane is used. In place of n-hexadecane, straight-run naphtha, diesel, or vacuum gas oils can also be used.

[0073] Figure 2 indicates the hydroprocessing catalyst was soaked with a sulphiding feed without a flow of hydrogen in the reactor and at ambient temperature for a period of 3 hours (ending at time 3.5 hours after zero time in Figure 2). Catalyst soaking provides for complete wetting of the hydroprocessing catalyst; however, soaking is optional. Liquid was drained from the bottom of a downstream gas liquid separator.

[0074] After introducing the sulphiding feed to the reactor, the hydroprocessing reactor bed temperature was raised to 250 °C at a rate of 30 °C per hour with a flow of H₂ at a ratio of 200NL H₂/L liquid feed. As shown in Figure 2, the temperature was increased from a time of 3.5 hours to a time of 10.8 hours after zero time.

[0075] The hydroprocessing reactor bed temperature was then held at 250 °C for a period of 8 hours. As shown in Figure 2, the temperature was held from a time of 10.8 hours to a time of 18.8 hours after zero time.

[0076] After holding the bed temperature, the bed temperature was further increased to 320 °C to 350 °C at a rate of 20 °C per hour without any temperature overshoot at the final temperature. As shown in Figure 2, the temperature was increased from a time of 18.8 hours to a time of 22.3 hours after zero time.
The hydroprocessing reactor bed temperature was then maintained at 320 °C to 350 °C for a period of 8 hours. As shown in Figure 2, the temperature was maintained at 320 °C to 350 °C from a time of 22.3 hours to a time of 30.0 hours after zero time.

During the step of maintaining the temperature at 320 °C to 350 °C for 8 hours, after 5 hours of maintaining the temperature at 320 °C to 350 °C, gas sampling began, and a first gas sample was obtained from the reactor effluent. A second gas sample was obtained close to 8 hours while the bed temperature is maintained at 320 °C to 350 °C. The first and second gas samples were analyzed in a refinery gas analyzer (RGA) gas chromatograph and constancy of H$_2$S concentration in reactor effluent gases in the first and second samples signified further uptake of sulphur on the catalyst did not take place. This marked the completion of the catalyst sulphiding process. If the first and second samples had not exhibited constancy in H$_2$S concentration, additional samples would have been taken and the temperature maintained until two successive samples exhibited constancy in H$_2$S concentration.

The present disclosure is further illustrated by the following embodiments, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort can be had to various other aspects, embodiments, modifications, and equivalents thereof which, after reading the description herein, can be suggest to one of ordinary skill in the art without departing from the spirit of the present invention or the scope of the appended claims.

**ADDITIONAL DISCLOSURE**

The following are enumerated embodiments which are provided as non-limiting examples:

A first embodiment, which is a process for dechlorination of a hydrocarbon stream comprising:

contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen to yield a hydrocarbon product, wherein the hydrocarbon stream comprises one or more chloride compounds in a concentration of 5 ppm or more based on a total weight of the hydrocarbon stream; and

recovering a treated hydrocarbon stream from the hydrocarbon product, wherein the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration of less than 5 ppm based on a total weight of the treated hydrocarbon stream.

A second embodiment, which is the process of the first embodiment, wherein the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration of less than 1 ppm based on the total weight of the treated hydrocarbon stream.

A third embodiment, which is the process of any one of the first through the second embodiments, wherein the hydrocarbon stream comprises the one or more chloride compounds in a concentration of greater than 200 ppm based on a total weight of the hydrocarbon stream.
[0084] A fourth embodiment, which is the process of any one of the first through the third embodiments, wherein the hydrocarbon stream further comprises one or more olefins, wherein the treated hydrocarbon stream further comprises the one or more olefins in a concentration of less than 1 wt% based on the total weight of the treated hydrocarbon stream.

[0085] A fifth embodiment, which is the process of the fourth embodiment, wherein the one or more olefins are present in the hydrocarbon stream in a concentration of 20 wt% or more based on the total weight of the hydrocarbon stream.

[0086] A sixth embodiment, which is the process of any one of the fourth through the fifth embodiments, wherein the concentration of the one or more olefins in the treated hydrocarbon stream is less than the concentration of the one or more olefins in the hydrocarbon stream due to hydrogenation of at least a portion of the one or more olefins from the hydrocarbon stream during the step of contacting.

[0087] A seventh embodiment, which is the process of any one of the first through the sixth embodiments, wherein the hydrocarbon stream is one or more of a plastic pyrolysis oil and a tire pyrolysis oil.

[0088] An eighth embodiment, which is the process of any one of the first through the seventh embodiments, wherein the hydrocarbon stream further comprises paraffins.

[0089] A ninth embodiment, which is the process of the eighth embodiment, wherein the hydrocarbon stream further comprises one or more olefins, wherein the treated hydrocarbon stream further comprises the paraffins and the one or more olefins, wherein the one or more olefins of the treated hydrocarbon stream are present in a concentration of less than 1 wt% based on the total weight of the treated hydrocarbon stream.

[0090] A tenth embodiment, which is the process of any one of the first through third and eighth embodiments, wherein the hydrocarbon stream comprises no olefins.

[0091] An eleventh embodiment, which is the process of any one of the first through the tenth embodiments, further comprising:

   adding one or more sulphides to the hydrocarbon stream before the step of contacting.

[0092] A twelfth embodiment, which is the process of the eleventh embodiment, wherein the one or more sulphides are added to the hydrocarbon stream in an amount such that a sulphur content in the hydrocarbon stream is about 0.5 wt% to about 5 wt% based on the total weight of the hydrocarbon stream.

[0093] A thirteenth embodiment, which is the process of any one of the first through the twelfth embodiments, wherein the hydrocarbon stream further comprises one or more sulphides.
[0094] A fourteenth embodiment, which is the process of the thirteenth embodiment, wherein the one or more sulphides of the hydrocarbon stream are present in an amount such that a sulphur content of the hydrocarbon stream is about 0.5 wt% to about 5 wt% based on the total weight of the hydrocarbon stream.

[0095] A fifteenth embodiment, which is the process of any one of the first through the fourteenth embodiments, wherein the hydrotreating catalyst comprises cobalt and molybdenum on an alumina support, nickel and molybdenum on an alumina support, or nickel and molybdenum sulphides.

[0096] A sixteenth embodiment, which is the process of any one of the first through the fifteenth embodiments, wherein contacting the hydrocarbon stream with the hydrotreating catalyst comprises: contacting one or more sulphides contained in or added to the hydrocarbon stream with the hydrotreating catalyst.

[0097] A seventeenth embodiment, which is the process of the sixteenth embodiment, wherein the one or more sulphides are contained in or added to the hydrocarbon stream in an amount such that a sulphur content of the hydrocarbon stream is about 2 wt% based on the total weight of the hydrocarbon stream.

[0098] An eighteenth embodiment, which is the process of any one of the first through the seventeenth embodiments, wherein the step of contacting is performed at a temperature of 100 °C to 450 °C.

[0099] A nineteenth embodiment, which is the process of any one of the first through the eighteenth embodiments, wherein the step of contacting is performed at a temperature of 100 °C to 350 °C.

[0100] A twentieth embodiment, which is the process of any one of the first through the nineteenth embodiments, wherein the step of contacting is performed at a temperature of 260 °C to 350 °C.

[0101] A twenty-first embodiment, which is the process of any one of the first through the twentieth embodiments, wherein the hydrocarbon stream is in a liquid phase.

[0102] A twenty-second embodiment, which is the process of any one of the first through the twenty-first embodiments, wherein the step of contacting is performed at a weight hourly space velocity of 0.1 to 10 hr⁻¹.

[0103] A twenty-third embodiment, which is the process of any one of the first through the twenty-second embodiments, wherein the step of contacting is performed at a hydrogen to hydrocarbon ratio of 10 to 3,000 NL/L.

[0104] A twenty-fourth embodiment, which is the process of any one of the first through the twenty-third embodiments, wherein the step of contacting is performed at a pressure of 1 to 200 barg.

[0105] A twenty-fifth embodiment, which is the process of any one of the first through the twenty-fourth embodiments, wherein the treated hydrocarbon stream comprises the one or more chloride
compounds in a concentration of less than 3 ppm based on a total weight of the treated hydrocarbon, the process further comprising:

feeding the treated hydrocarbon stream to a steam cracker.

[00106] A twenty-sixth embodiment, which is the process of any one of the first through the twenty-fifth embodiments, further comprising:

blending the treated hydrocarbon stream with a non-chlorinated hydrocarbon stream to yield a blended hydrocarbon stream comprising the one or more chloride compounds in a concentration of less than 3 ppm based on a total weight of the blended hydrocarbon stream; and

feeding the blended hydrocarbon stream to a steam cracker.

[00107] A twenty-seventh embodiment, which is the process of any one of the first through the twenty-sixth embodiments, wherein recovering a treated hydrocarbon stream from the hydrocarbon product comprises:

separating a treated product from a chlorine-containing gas in a separator; and

flowing the treated product in the treated hydrocarbon stream from the separator.

[00108] A twenty-eighth embodiment, which is the process of any one of the first through the twenty-seventh embodiments, wherein no hydrogen halides and no halogenated organic compounds are recycled to the hydroprocessing reactor.

[00109] A twenty-ninth embodiment, which is the process of any one of the first through the twenty-eighth embodiments, wherein the step of contacting is performed without use of chlorine sorbents.

[00110] A thirtieth embodiment, which is the process of any one of the first through the twenty-ninth embodiments, wherein the step of contacting is performed without the presence of Na₂C0₃ in an effective amount to function as a dechlorinating agent.

[00111] A thirty-first embodiment, which is the process of any one of the first through the thirtieth embodiments, wherein the hydroprocessing reactor is configured to operate in the slurry phase.

[00112] A thirty-second embodiment, which is the process of any one of the first through the thirty-first embodiments, wherein the step of contacting includes simultaneous dechlorination and hydrogenation of the hydrocarbon stream such that the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration less than 1 ppm and one or more olefins in a concentration less than 1 wt% based on the total weight of the treated hydrocarbon stream.

[00113] A thirty-third embodiment, which is the process of any one of the first through the thirty-second embodiments, wherein the hydroprocessing catalyst is sulphided.

[00114] A thirty-fourth embodiment, which is the process of any one of the first through the thirty-third embodiments, wherein the one or more chloride compounds include chlorine-containing hydrocarbons.
A thirty-fifth embodiment, which is the process of the thirty-fourth embodiment, wherein the chlorine-containing hydrocarbons include aliphatic chlorine-containing hydrocarbons, aromatic chlorine-containing hydrocarbons, other hydrocarbons containing chlorides, or a combination of any of aliphatic chlorine-containing hydrocarbons, aromatic chlorine-containing hydrocarbons, and other hydrocarbons containing chlorides.

A thirty-sixth embodiment, which is the process of any one of the thirty-fourth through the thirty-fifth embodiments, wherein the chlorine-containing hydrocarbons include 1-chlorohexane, 2-chloropentane, 3-chloro-3-methyl pentane, (2-chloroethyl) benzene, chlorobenzene, or combinations thereof.

While embodiments of the disclosure have been shown and described, modifications thereof can be made without departing from the spirit and teachings of the invention. The embodiments and examples described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the detailed description of the present invention. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference.
CLAIMS

What is claimed is:

1. A process for dechlorination of a hydrocarbon stream comprising:
   contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen to
   yield a hydrocarbon product, wherein the hydrocarbon stream comprises one or more chloride compounds
   in a concentration of 5 ppm or more based on a total weight of the hydrocarbon stream; and
   recovering a treated hydrocarbon stream from the hydrocarbon product, wherein the treated
   hydrocarbon stream comprises the one or more chloride compounds in a concentration of less than 5 ppm
   based on a total weight of the treated hydrocarbon stream.

2. The process of claim 1, wherein the treated hydrocarbon stream comprises the one or more chloride
   compounds in a concentration of less than 1 ppm based on the total weight of the treated hydrocarbon
   stream.

3. The process of claim 1, wherein the hydrocarbon stream comprises the one or more chloride
   compounds in a concentration of greater than 200 ppm based on a total weight of the hydrocarbon stream.

4. The process of claim 1, wherein the hydrocarbon stream further comprises one or more olefins,
   wherein the treated hydrocarbon stream further comprises the one or more olefins in a concentration of
   less than 1 wt% based on the total weight of the treated hydrocarbon stream.

5. The process of claim 4, wherein the one or more olefins are present in the hydrocarbon stream in a
   concentration of 20 wt% or more based on the total weight of the hydrocarbon stream.

6. The process of claim 1, wherein the hydrocarbon stream further comprises paraffins.

7. The process of claim 6, wherein the hydrocarbon stream further comprises one or more olefins,
   wherein the treated hydrocarbon stream further comprises the paraffins and the one or more olefins,
   wherein the one or more olefins of the treated hydrocarbon stream are present in a concentration of less
   than 1 wt% based on the total weight of the treated hydrocarbon stream.

8. The process of claim 1, wherein the hydrocarbon stream further comprises one or more sulphides,
   wherein the one or more sulphides of the hydrocarbon stream are present in an amount such that a sulphur
   content of the hydrocarbon stream is about 0.5 wt% to about 5 wt% based on the total weight of the
   hydrocarbon stream.

9. The process of claim 1, wherein the hydroprocessing catalyst comprises cobalt and molybdenum on
   an alumina support, nickel and molybdenum on an alumina support, or nickel and molybdenum sulphides,
   wherein contacting the hydrocarbon stream with the hydroprocessing catalyst comprises:
   contacting one or more sulphides contained in or added to the hydrocarbon stream with the
   hydroprocessing catalyst, and wherein the one or more sulphides are contained in or added to the
hydrocarbon stream in an amount such that a sulphur content of the hydrocarbon stream is about 2 wt% based on the total weight of the hydrocarbon stream.

10. The process of claim 1, wherein the step of contacting is performed at a temperature of 100 °C to 450 °C.

11. The process of claim 1, wherein the step of contacting is performed at a weight hourly space velocity of 0.1 to 10 hr⁻¹, at a hydrogen to hydrocarbon ratio of 10 to 3,000 NL/L, and at a pressure of 1 to 200 barg.

12. The process of claim 1, wherein the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration of less than 3 ppm based on a total weight of the treated hydrocarbon, the process further comprising:

   feeding the treated hydrocarbon stream to a steam cracker.

13. The process of claim 1, further comprising:

   blending the treated hydrocarbon stream with a non-chlorinated hydrocarbon stream to yield a blended hydrocarbon stream comprising the one or more chloride compounds in a concentration of less than 3 ppm based on a total weight of the blended hydrocarbon stream; and

   feeding the blended hydrocarbon stream to a steam cracker.

14. The process of claim 1, wherein recovering a treated hydrocarbon stream from the hydrocarbon product comprises:

   separating a treated product from a chlorine-containing gas in a separator; and

   flowing the treated product in the treated hydrocarbon stream from the separator.

15. The process of claim 1, wherein no hydrogen halides and no halogenated organic compounds are recycled to the hydroprocessing reactor.

16. The process of claim 1, wherein the step of contacting is performed without use of chlorine sorbents.

17. The process of claim 1, wherein the step of contacting is performed without the presence of Na₂CO₃ in an effective amount to function as a dechlorinating agent.

18. The process of claim 1, wherein the hydroprocessing reactor is configured to operate in the slurry phase.

19. The process of claim 1, wherein the step of contacting includes simultaneous dechlorination and hydrogenation of the hydrocarbon stream such that the treated hydrocarbon stream comprises the one or more chloride compounds in a concentration less than 1 ppm and one or more olefins in a concentration less than 1 wt% based on the total weight of the treated hydrocarbon stream.
20. The process of claim 1, wherein the one or more chloride compounds include 1-chlorohexane, 2-chloropentane, 3-chloro-3-methyl pentane, (2-chloroethyl) benzene, chlorobenzene, or combinations thereof.
1. H₂ purge for 30-60 mins at 40-60 barg at ambient temperature
2. Stop H₂
3. Pump sulfiding feed for 3 hrs at 3hr⁻¹ WHSV, without H₂, purge at 40-60 barg at ambient temperature
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELD SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C1OG

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>US 2014/275680 Al (ZHAN BI-ZENG [US] ET AL) 18 September 2014 (2014-09-18) example 5; table 3 examples 3-4; table 2</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

  * "A" document defining the general state of the art which is not considered to be of particular relevance
  * "E" earlier application or patent but published on or after the international filing date
  * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  * "O" document referring to an oral disclosure, use, exhibition or other means
  * "P" document published prior to the international filing date but later than the priority date claimed

  * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  * "A" document member of the same patent family

**Date of the actual completion of the international search**

9 May 2016

**Date of mailing of the international search report**

13/05/2016

Name and mailing address of the ISA:

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Fax: (+31-70) 340-3016

Authorized officer

Bernet, Olivier
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