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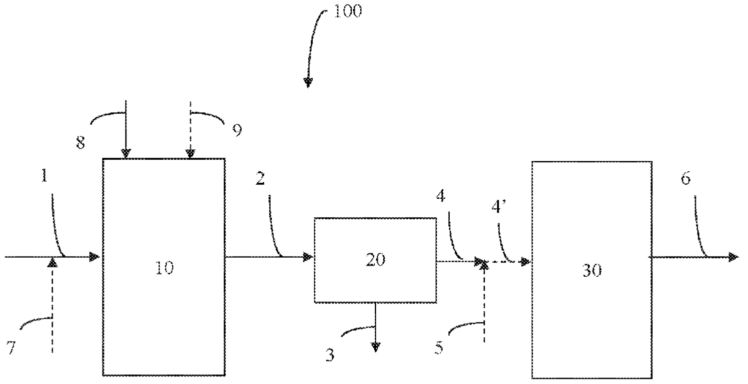


FIG. 1

(57) Abstract: A process for activating and maintaining a catalyst for use in hydrocracking a hydrocarbon stream includes continuously contacting a hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen. Sulphides and chloride compounds in the hydrocarbon stream are used such that the hydroprocessing catalyst has the ability to hydrogenate, dechlorinate, and hydrocrack components of the hydrocarbon stream.

PROCESS FOR PREPARATION OF HYDROCRACKING CATALYST FOR USE IN HYDROCRACKING OF HYDROCARBON STREAMS

TECHNICAL FIELD

[0001] The present disclosure relates to the preparation of hydrocracking catalysts for the treatment of hydrocarbon streams resulting from pyrolysis of waste plastics for use in downstream processes.

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, olefin content less than 1 wt%, and boiling end point requirements of 370 °C.

SUMMARY

[0003] Disclosed herein is a process for activating and maintaining a catalyst for use in hydrotreating a hydrocarbon stream to simultaneously reduce heavier boiling components, chlorides, and olefins, comprising continuously contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen, wherein the hydrocarbon stream comprises one or more chloride compounds and one or more sulphides.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Figure 1 illustrates a hydroprocessing system which utilizes the hydrocracking catalyst prepared as described herein for hydrocracking, hydrogenating, and dechlorinating components of 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 preparing a hydrocracking catalyst for use in hydrocracking hydrocarbon streams. The embodiments involve activating and maintaining a catalyst for use in hydrocracking a hydrocarbon stream. Generally, the process includes continuously contacting a hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen, where the hydrocarbon stream comprises one or more chloride compounds and one or more sulphides. In certain embodiments, before the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst in the presence of hydrogen, the process may include contacting a catalyst activating stream with the hydroprocessing catalyst, wherein the catalyst activating stream comprises one or more sulphides.

[0011] Embodiments of the process for preparing a hydrocracking catalyst are described in context with reference to Figure 1. Figure 1 illustrates a hydroprocessing system 100 which utilizes the hydrocracking catalyst prepared as described herein for hydrocracking components of a hydrocarbon stream 1 to levels suitable for introduction to a steam cracker 30. In additional embodiments, the hydroprocessing catalyst is used for dechlorinating chloride compounds and hydrogenating olefins contained in a hydrocarbon stream 1 to levels suitable for introduction to the steam cracker 30.

[0012] The hydroprocessing 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.

[0013] 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.

[0014] The hydrocarbon stream 1 generally includes one or more hydrocarbons, at least a portion of which are heavy hydrocarbon molecules. In embodiments, the hydrocarbon stream 1 may additionally include one or more sulphides, one or more chloride compounds, hydrogen, or combinations thereof. The hydrocarbon stream 1 is generally in a liquid phase. A hydrogen (H_2) stream can be added to hydrocarbon stream 1 before entering the hydroprocessing reactor 10. Optionally, a H_2 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 H_2.

[0015] 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.

[0016] 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.

[0017] 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, C_1 to C_{22} 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. In embodiments, at least a portion of the paraffins in the hydrocarbon stream 1 comprises at least a portion of the heavy hydrocarbon molecules.

[0018] 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, C_2 to C_{10} 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. In embodiments, at least a portion of the one or more olefins in the hydrocarbon stream 1 comprise at least a portion of the heavy hydrocarbon molecules. 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.

[0019] In an embodiment, the hydrocarbon stream 1 comprises no olefins.

[0020] 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. In embodiments, at least a portion of the naphthenes in the hydrocarbon stream 1 comprise at least a portion of the heavy hydrocarbon molecules.

[0021] 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. In embodiments, at least a portion of the aromatics in the hydrocarbon stream 1 comprise at least a portion of the heavy hydrocarbon molecules. 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.

[0022] In an embodiment, the hydrocarbon stream 1 comprises no aromatic hydrocarbons.

[0023] As discussed herein, embodiments of the processes disclosed herein contemplate hydrocracking of molecules, and in particular, heavy hydrocarbon molecules of the hydrocarbon stream 1. In an embodiment, the concentration of heavy hydrocarbon molecules 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 the heavy hydrocarbon molecules in the hydrocarbon stream 1 may be 10 wt% to 90 wt% based on the total weight of the hydrocarbon stream 1. As described above, the heavy hydrocarbon molecules may include paraffins, i-paraffins, olefins, naphthenes, aromatic hydrocarbons, or combinations thereof. In embodiments, the heavy hydrocarbon molecules may include C_{16} and larger hydrocarbons. Greater than 5, 10, 15, 20, 25, 30 wt% or more of the heavy hydrocarbon molecules in the hydrocarbon stream 1 is hydrocracked when the hydrocarbon stream 1 is contacted with the hydroprocessing catalyst in the hydroprocessing reactor 10.

[0024] 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, 2-chloropentane, 3-chloro-3-methyl pentane, (2-chloroethyl) benzene, chlorobenzene, 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.

[0025] Sulphides which may be included in the hydrocarbon stream 1 include sulphur-containing compounds. For example, a sulphiding agent such as dimethyl disulphide ($C_2H_6S_2$), dimethyl sulphide (C_2H_6S), mercaptans (R-SH), carbon disulphide (CS_2), hydrogen sulphide (H_2S), or combinations thereof may be used as the sulphide in the hydrocarbon stream 1.

[0026] In an embodiment, one or more sulphides (e.g., dimethyl disulphide ($C_2H_6S_2$), dimethyl sulphide (C_2H_6S), mercaptans (R-SH), carbon disulphide (CS_2), hydrogen sulphide (H_2S), 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.

[0027] 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.

[0028] 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 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.

[0029] 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.

[0030] In embodiments, the hydrocarbon stream 1 may be one or more 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 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). It is contemplated that for embodiments having one or more plastic pyrolysis oils in the hydrocarbon stream 1, at least a portion of the plastic pyrolysis oils comprises heavy hydrocarbon molecules (e.g., also referred to as heavy ends of the pyrolysis oils).

Hydrocracking of the heavy ends of the plastic pyrolysis oils to meet steam cracker 30 specifications is contemplated.

[0031] 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.

[0032] 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.

[0033] The hydroprocessing reactor 10 is configured to hydrocrack, and in some embodiments, additionally dechlorinate and 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 H_2 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.

[0034] 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, reactions in the hydroprocessing reactor 10 may cause a rupture of a bond of an organic compound, resulting in “cracking” of a hydrocarbon molecule into two or more smaller hydrocarbon molecules, or resulting in 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), hydrocracking of large paraffins or i-paraffins to smaller hydrocarbon molecules, hydrocracking of aromatic hydrocarbons to smaller cyclic or acyclic hydrocarbons, conversion of one or more aromatic compounds 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.

[0035] 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 stream may then be treated as described herein for stream 2.

[0036] In an embodiment, the hydroprocessing reactor 10 may comprise one or more vessels.

[0037] In embodiments of a single vessel or multiple vessels, the sulphur present in the hydrocarbon stream 1 is removed as H_2S to provide a reduced level of sulphur acceptable for downstream processing in steam crackers and refinery units.

[0038] 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.

[0039] 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 barg to 200 barg; or alternatively, 20 barg to 60 barg. 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 (H_2/HC) flow ratio of 10 to 3,000 NL /L; or alternatively, 200 to 800 NL /L.

[0040] 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 Na_2CO_3 in an effective amount to function as a dechlorinating agent, or both.

[0041] To prepare the hydrocracking catalyst, any hydroprocessing catalyst used for hydrogenation (e.g., saturation) of olefins and aromatic hydrocarbons (e.g., a commercially available hydrotreating catalyst) may be used. 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.

[0042] In embodiments where the hydrocarbon stream 1 comprises one or more sulphides and one or more chloride compounds, contacting the hydrocarbon carbon stream 1 with the hydroprocessing catalyst acts to activate the hydroprocessing catalyst by sulphiding and to acidify the hydroprocessing catalyst by chlorinating. Continuously contacting the hydroprocessing catalyst with the hydrocarbon stream 1 containing the one or more sulphides, the one or more chloride compounds, or both, may maintain the catalyst activity on a continuous basis. Activating and maintaining the activation of the hydroprocessing catalyst in effect transforms the functionality of the hydroprocessing catalyst to also exhibit hydrocracking ability, e.g., the hydroprocessing catalyst transforms to a hydrocracking catalyst which maintains a hydrogenating ability.

[0043] In embodiments, the hydroprocessing catalyst is activated and/or the activity is maintained by sulphiding the hydroprocessing catalyst in-situ. For example, the hydroprocessing catalyst may be sulphided (i.e., activated) and/or sulphiding (i.e., maintaining 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 compounds 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.

[0044] 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, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30 or fewer 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 the 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.

[0045] In embodiments, sulphiding and maintaining the catalyst in sulphided form may use two different concentrations of sulphur content in the hydrocarbon stream 2. For example, the one or more sulphides may be included (e.g., provided via spiking stream 7) in the hydrocarbon stream 2 in an amount such that the sulphur content of the hydrocarbon stream 1 is about 2 wt% based on the total weight of the hydrocarbon stream 2 for sulphiding, and the one or more sulphides may be maintained (e.g., via spiking stream 7) in the hydrocarbon stream 2 in an amount such that the sulphur content of the hydrocarbon stream 1 is about 2 wt% based on the total weight of the hydrocarbon stream 2 for maintaining the hydroprocessing catalyst in the sulphided form. In another example, 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 3 wt% based on the total weight of the catalyst activating stream 9 for sulphiding, and the one or more sulphides may be included (e.g., via spiking stream 7) in the hydrocarbon stream 2 in an amount such that the sulphur content of the hydrocarbon stream 1 is about 2 wt% based on the total weight of the hydrocarbon stream 2 for maintaining the hydroprocessing catalyst in the sulphided form.

[0046] 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.

[0047] Sulphiding and maintaining the hydroprocessing catalyst in sulphided form result in a catalyst which has hydrogenation sites (sulphided metal) for hydrogenation of components of the hydrocarbon stream 1. Chloriding the hydroprocessing catalyst results in a catalyst which has hydrocracking sites (chlorided alumina) for hydrocracking components of the hydrocarbon stream 1. That is, chloriding the hydroprocessing catalyst transforms the catalyst into a hydrocracking catalyst (in addition to having hydrogenation capabilities).

[0048] 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.

[0049] 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 flowing the treated product in the treated hydrocarbon stream 4 from the separator 20.

[0050] 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.

[0051] 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.

[0052] 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.

[0053] In embodiments disclosed herein, no hydrogen halides and no halogenated organic compounds are recycled to the hydroprocessing reactor 10.

[0054] 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.

[0055] 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 yet 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 and hydrocracking 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.

[0056] 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. It is also contemplated that the concentration of aromatic hydrocarbons in the treated hydrocarbon stream 4 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 treated hydrocarbon stream 4 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 treated hydrocarbon product stream 4.

[0057] Due to hydrocracking of heavy hydrocarbon molecules when the hydrocarbon stream 1 is contacted with the hydroprocessing catalyst in the hydroprocessing reactor 10, the treated hydrocarbon stream 4 may have a boiling end point of 370 °C or less. A significant reduction in hydrocarbons boiling above 370 °C is obtained in stream 2 as compared to hydrocarbon stream 1.

[0058] 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.

[0059] 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%. Third, the steam cracker 30 requires the boiling end point of the stream fed to the steam cracker 30 to be 370 °C. 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.

[0060] The disclosed hydrocracking catalyst prepared according to the techniques disclosed herein both hydrocracks and hydrogenates components of a hydrocarbon stream fed to a hydroprocessing reactor 10 containing the catalyst. Moreover, chloride compounds contained in the hydrocarbon stream are removed. In embodiments, simultaneous hydrogenation, dechlorination, and hydrocracking of a hydrocarbon stream components is achieved in a single hydroprocessing step using the hydrocracking catalyst prepared as disclosed herein, with the treated hydrocarbon product being capable of feeding to a steam cracker having the feed requirements specified herein, without further separations or fractionations of the treated hydrocarbon product. Catalyst activity can be initiated and/or maintained simultaneously with the simultaneous hydrogenation, dechlorination, and hydrocracking by using hydrocarbon streams of the compositions disclosed herein which feed to a hydroprocessing reactor. The use of chloride compounds in the hydrocarbon stream 1 for activating and maintaining the activity of the hydrocracking catalyst in effect transforms the hydroprocessing catalyst to a hydrocracking catalyst.

[0061] As is demonstrated in the examples below and discussed above, it has been found that hydrocracking of olefins and heavy hydrocarbon molecules contained in a hydrocarbon stream occurs using a hydrocracking catalyst prepared using a hydroprocessing catalyst under the conditions disclosed herein.

Hydrocracking according to the embodiments disclosed herein can occur over the operating pressures disclosed herein for hydroprocessing reactor 10, including those low pressures demonstrated in the examples. Embodiments of the processes disclosed herein meet the boiling end point of 370 °C required for steam crackers. Moreover, the disclosed embodiments demonstrate that about 30 wt% of the heavy hydrocarbon molecules of a hydrocarbon stream can undergo hydrocracking at the conditions disclosed herein. When the hydrocarbon stream contains plastic pyrolysis oil, the heavier ends of the plastic pyrolysis oil are hydrocracked. Increased levels of paraffins due to the hydrocracking ability of the processes disclosed herein can result in a higher production of propylene in steam crackers. LPG gases are not liberated in the disclosed processes until the temperature of the one or more catalyst beds in the hydroprocessing reactor 10 reaches about 400 °C. Liquid feed to crackers is maximized, and as a result, gas product formation is minimized, which is useful for existing plants which are constrained on the gas flow rate to the gas compressor. In the disclosed embodiments, the production of methane and ethane is also low.

[0062] 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 hydroprocessing 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.

[0063] 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.

[0064] 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.

[0065] Thus, the disclosed processes achieve the requirements of chloride content, olefin content, and boiling end point of the feed for a steam cracker simultaneously.

EXAMPLES

[0066] 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.

[0067] Examples 1 to 6 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 1mm glass beads. The catalyst bed temperature was controlled to isothermal by varying the controlled furnace zone skin temperatures. The 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 H_2 gas was fed using a mass flow controller. The reactor effluent (i.e., the hydrocarbon product) gases 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

[0068] In Example 1, a hydrocarbon feed mixture was prepared by mixing 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. Dimethyl disulphide, 2-chloropentane, 3-chloro-3-methyl pentane, 1-chlorohexane, (2-chloroethyl) benzene, and chlorobenzene were then added to give 205 ppm organic chlorides and a sulphur content of 2 wt% S in the combined feed mixture. This combined feed mixture was used as the hydrocarbon stream which was contacted with the hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H_2 at conditions of 280 °C reactor temperature, 60 barg reactor pressure, 0.92 hr^{-1} WHSV, and 414 NL/L H_2/HC flow ratio. The liquid product (i.e., the treated hydrocarbon stream) was analyzed in a DHA wherein molecules lighter than C_{13} are injected into the GC column and heavier than C_{13} are flushed out. The normalized composition of liquid product as measured by DHA was paraffins (26.24 wt%), i-paraffins (17.28 wt%), olefins (0 wt%), naphthenes (33.61 wt%), and aromatics (22.88 wt%). SIMDIS analysis of liquid product indicates that 78 wt% of the liquid product boils at 180 °C, and immediately at 79 wt%, the boiling point shifts to 286 °C; indicating that 22 wt% (i.e. 100-78 = 22) of the liquid product is hexadecane. This implies out of 30 wt% hexadecane in the feed (calculated based on the feed excluding chloride and sulphides, since dimethyl disulphide is converted to gases, the chloride compounds are dechlorinated so as to contribute less than 0.5 wt% of the product), 8 wt% of hexadecane was hydrocracked to lower products. As mentioned before, this 22 wt% does not get analyzed in DHA. This 22 wt% hexadecane unaccounted in DHA composition is added to the liquid product analyzed by DHA (DHA composition multiplied by 0.78 fraction that was injected into DHA) and the resulting composition of the liquid product is 42.47 wt% paraffins, 13.48 wt% i-paraffins, 0 wt% olefins, 26.21 wt% naphthenes and 17.84 wt% aromatics. In addition, the chloride content of the liquid product was 0.09 ppmw.

[0069] Example 1 demonstrates it is possible to simultaneously dechlorinate, hydrogenate, and hydrocrack a PIONA hydrocarbon stream containing heavy hydrocarbon molecules (e.g., hexadecane), a chloride content of more than 200 ppm, and an olefin content of 20 wt% (calculated based on the feed excluding chloride and sulphides) such that a portion of the heavy hydrocarbon molecules are hydrocracked, chloride content is reduced to less than 1 ppm, and olefins are completely removed (0 wt% in the liquid product). Comparing feed and liquid product compositions, it can be said that paraffins, i-paraffins, and naphthenes have increased in concentration, while aromatics have reduced in concentration and olefins were completely depleted. This clearly indicates hydrocracking of hexadecane as well as hydrocracking of olefins in feed. Thus, Example 1 additionally demonstrates olefins are hydrocracked in addition to being hydrogenated.

[0070] The DHA analysis summary by carbon number for the liquid product is shown below:

Carbon No.	n-Paraffins, wt%	i-Paraffins, wt%	Olefins, wt%	Naphthenes, wt%	Aromatics, wt%	Total, wt%
2						
3						
4		0.015				0.015
5	0.012					0.012
6	0.016	0.18		27.136	0.048	27.217

Carbon No.	n-Paraffins, wt%	i-Paraffins, wt%	Olefins, wt%	Naphthenes, wt%	Aromatics, wt%	Total, wt%
7						0
8	0.145	14.226		0.547	21.979	36.896
9		0.079		5.901	0.834	6.814
10	26.01	2.93				0.039
11						
12						
Total, wt%	26.221	17.268		35.584	22.86	99.933
Unknown						0.053
Heavies						0.013

EXAMPLE 2

[0071] Example 2 explores the effect of operating pressure on hydrocracking performance. A hydrocarbon feed mixture was prepared by mixing 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. Dimethyl disulphide, 2-chloropentane, 3-chloro-3-methyl pentane, 1-chlorohexane, (2-chloroethyl) benzene, and chlorobenzene were then added to give 205 ppm organic chlorides and a sulphur content of 2 wt% S in the combined feed mixture. This combined feed mixture 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 H_2 at conditions of 300 °C reactor temperature, 0.92 hr^{-1} WHSV, and 414 NL/L H_2/HC flow ratio. Three different pressure conditions were studied: 60 barg for Example 2A, 20 barg for Example 2B, and 10 barg for Example 2C. The liquid products (i.e., the treated hydrocarbon streams) for each of Examples 2A to 2C were analyzed using SIMDIS, and the results are shown below:

Example 2A Liquid Product		**Example 2B Liquid Product**		**Example 2C Liquid Product**	
60 barg		**20 barg**		**10 barg**	
Cut, wt%	**T, °C**	**Cut, wt%**	**T, °C**	**Cut, wt%**	**T, °C**
0	61.4	0	52.0	0	61.4
5	72.0	5	61.4	5	72.0
10	72.0	10	72.0	10	72.0
15	72.0	15	72.0	15	72.0
20	72.0	20	72.0	20	72.0
25	72.0	25	72.0	25	72.0
30	87.6	30	72.0	30	72.0
35	87.6	35	72.0	35	87.6
40	87.6	40	87.6	40	87.6
45	87.6	45	87.6	45	132.0
50	87.6	50	134.6	50	137.2
55	129.4	55	137.2	55	139.8
60	134.6	60	139.8	60	139.8
65	139.8	65	142.4	65	161.2
70	170.6	70	163.2	70	173.8
75	176.0	75	175.4	75	177.0

Example 2A Liquid Product		Example 2B Liquid Product		Example 2C Liquid Product	
60 barg		20 barg		10 barg	
Cut, wt%	T, °C	Cut, wt%	T, °C	Cut, wt%	T, °C
79	177.6	80	179.0	78	178.0
80	278.6	83	180.6	80	271.6
85	289.2	85	279.6	85	288.2
90	292.0	90	291.0	90	291.6
95	294.0	95	294.6	95	294.0
99	295.4	99	296.8	99	295.4
100	295.6	100	297.0	100	295.6

[0072] The DHA analysis summary of the liquid product boiling below 240 °C is shown below:

Example No.	n-Paraffins, wt%	i-Paraffins, wt%	Olefins, wt%	Naphthenes, wt%	Aromatics, wt%	Unknown, wt%	Heavies, wt%
2A	22.507	19.415	0.183	31.159	17.912	0.131	0.693
2B	19.544	21.513	0.047	30.490	27.465	0.315	0.626
2C	21.368	21.281	0.000	24.687	30.719	0.355	1.591

[0073] The results provided in the tables above indicate that 20 wt% or less of the liquid product for each of Examples 2A to 2C boils in the hexadecane boiling point range. In contrast, the feed contained 30 wt% hexadecane (calculated based on the feed excluding chlorides and sulphides). Hence, at all pressures, hydrocracking of heavy hydrocarbon molecules (e.g., hexadecane) using a hydrogenation catalyst is demonstrated.

[0074] The corresponding chloride contents of the liquid product (i.e., treated hydrocarbon stream) at 60 barg, 20 barg, and 10 barg were respectively 0.11 ppmw, 0.09 ppmw, and 0.12 ppmw.

[0075] The liquid product (analyzed in DHA) for Example 2A (60 barg) contained 0.183 wt% olefins, for Example 2B (20 barg) contained 0.047 wt%, and for Example 2C (10 barg) contained 0 wt% olefins. At lower pressures, a significant increase in aromatics is observed.

[0076] Example 2 demonstrates it is possible to simultaneously dechlorinate and hydrocrack a PIONA hydrocarbon stream containing heavy hydrocarbon molecules (e.g., hexadecane) and a chloride content of more than 200 ppmw such that a portion of the heavy hydrocarbon molecules are hydrocracked and chloride content is reduced to less than 1 ppm for all pressures tested.

EXAMPLE 3

[0077] 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 sulphided hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H_2 at conditions of 260 °C reactor temperature, 60 barg reactor pressure, 0.92 hr^{-1} WHSV and 414 NL/L H_2/HC flow ratio. The liquid product (i.e., the treated hydrocarbon stream) contained 0.1 ppmw chloride.

[0078] Example 3 demonstrates the effective removal of chloride compounds from a hydrocarbon stream at very low temperatures.

EXAMPLE 4

[0079] In Example 4, 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 hydroprocessing catalyst in the packed bed reactor as mentioned above in the presence of H_2 under several operating conditions as provided in the table below:

T, °C	**P, barg**	**WHSV, hr^{-1}**	**H_2/HC, NL/L**	**Cl, ppm in liquid product**
300	60	0.92	414	0.32
300	40	0.92	414	0.87
350	40	0.92	414	3.42
400	40	0.92	414	3.15

[0080] The gas composition for the reactor effluents is shown below.

T, °C	**P, barg**	**WHSV, hr^{-1}**	**H_2/HC, NL/L**	**Cl, ppm in liquid product**	**H_2, mole %**	**CH_4, mole %**	**C_2H_6, mole %**	**C_3H_8, mole %**	**n-C_4H_{10}, mole%**	**i-C_4H_{10}, mole%**
300	40	0.92	414	0.87	96.63	3.25	0.12	-	-	-
350	40	0.92	414	3.42	95.32	4.48	0.2	-	-	-
400	40	0.92	414	3.15	93.96	5.21	0.45	0.23	0.08	0.07

[0081] As can be seen, the data indicates LPG gases are formed at temperatures close to 400 °C.

[0082] Example 4 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 ppmw chlorides to less than 5 ppmw 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 4 demonstrates removal of chloride compounds to chloride contents less than 3 ppmw, and even sub-ppm levels.

EXAMPLE 5

[0083] In Example 5, a hydrocarbon feed mixture was prepared by mixing 30 wt% n-hexadecane, 10 wt% i-octane, 20 wt% 1-decene, 20 wt% cyclohexane, and 20 wt% ethyl benzene. Dimethyl disulphide, 2-chloropentane, 3-chloro-3-methyl pentane, 1-chlorohexane, (2-chloroethyl) benzene, and chlorobenzene were then added to give 1100ppm organic chlorides and a sulphur content of 2 wt% S in the combined feed mixture. This combined feed mixture was used as the hydrocarbon stream which was contacted with the hydrogenating catalyst in the packed bed reactor as mentioned above in the presence of H_2 at conditions of 300 °C reactor temperature, 40 barg reactor pressure, 0.92 hr^{-1} WHSV, and 414 NL/L H_2/HC flow ratio. The liquid product contained 0.23 ppmw chlorides and paraffins of 22.569 wt%, i-paraffins of 19.752 wt%, olefins of 0.114 wt%, naphthenes of 33.242 wt%, aromatics of 23.7 wt%, unknowns of 0.16wt% and heavies of 0.463 wt% as per DHA analysis. This again demonstrates the dechlorination of liquid at much higher chloride concentrations.

[0084] The SIMDIS of liquid product resulted in the following distribution and also indicated hydrocracking:

Cut, wt%	**T, °C**
0	61.4
5	72
10	72
15	72
20	72
25	72
30	72
35	72
40	87.6
45	87.6
50	132
55	134.6
60	137.2
65	142.4
70	170.6
75	175.4
80	177
85	287
90	290
95	292.2
99	293.4
100	293.8

[0085] DHA Group type analysis of the liquid product by carbon number (in wt%) is as below:

Carbon No.	n-Paraffins, wt%	i-Paraffins, wt%	Olefins, wt%	Naphthenes, wt%	Aromatics, wt%	Total, wt%
2						0
3						0
4	0.008	0.056				0.064
5	0.033	0.021				0.054
6	0.035	0.05		26.925	0.072	27.082
7	0.013	0.008		0.012		0.033
8	0.287	13.892		0.951	21.97	37.1
9		0.172	0.114	5.265	1.623	7.174
10	22.161	5.553		0.089	0.035	27.838
11	0.025					0.025
12	0.007					0.007
					Oxygenates	
					Heavies	0.464
					Unknown	0.16
					Total, wt%	100.001

[0086] In this example, the yield of liquid products was 95.5wt% of the total products. The balance was gas products.

EXAMPLE 6

[0087] In Example 6, a n-hexadecane feed mixture was prepared by mixing n-hexadecane with dimethyl disulphide, 2-chloropentane, 3-chloro-3-methyl pentane, 1-chlorohexane, (2-chloroethyl) benzene, and chlorobenzene to give 1,034 ppm of chlorides and 2 wt% Sulphur in the feed. This combined feed mixture was used as the hydrocarbon stream which was contacted with the hydrogenating catalyst in the packed bed reactor as mentioned above in the presence of H_2 at conditions of 300 °C reactor temperature, 40 barg reactor pressure, 0.92 hr^{-1} WHSV, and 414 NL/L H_2/HC flow ratio. The liquid product contained 0.3 ppmw chlorides and paraffins of 22.569 wt%, i-paraffins of 19.752 wt%, olefins of 0.114 wt%, naphthenes of 33.242 wt%, aromatics of 23.7 wt%, unknowns of 0.16 wt% and heavies of 0.463 wt% as per DHA analysis. This again demonstrates the dechlorination of liquid at high chloride concentrations to sub-ppm levels.

[0088] The SIMDIS of liquid product resulted in the following distribution and also indicated hydrocracking to the extent of about 15 wt% on a chloride and sulphide-free feed basis:

Cut, wt%	T, °C
0	61.4
5	129.4
10	161.2
13	170.6
14	260.2

Cut, wt%	T, °C
15	272.4
20	285.2
25	287.4
30	289
35	290.2
40	291.2
45	292.2
50	293
55	293.8
60	294.4
65	295
70	295.6
75	296.2
80	297
85	297.4
90	297.8
95	298.2
99	298.8
100	310.8

[0089] DHA Group type analysis of the liquid product by carbon number (in wt%) is as below and indicates conversion of n-hexadecane to various PIONA components:

Carbon No.	n-Paraffins, wt%	i-Paraffins, wt%	Olefins, wt%	Naphthenes, wt%	Aromatics, wt%	Total, wt%
2	0.005					0.005
3	0.006					0.006
4	0.019	0.098				0.118
5	0.068	0.064				0.132
6	0.072	0.133		25.607	0.11	25.922
7	0.016	0.034				0.051
8	0.401	13.31		1.268	21.179	36.157
9		0.133	0.136	5.53	2.449	8.248
10	19.165	8.19		0.213	0.049	27.617
11	0.03					0.03
12	0.011					0.011
					Oxygenates	
					Heavies	1.413
					Unknown	0.29
					Total, wt%	100

EXAMPLE 7

[0090] Example 7 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.

[0091] 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).

[0092] After purging the hydroprocessing reactor for 30-60 minutes at ambient temperature, the hydrogen purge was stopped.

[0093] 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.

[0094] 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.

[0095] 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 H_2 at a ratio of 200NL H_2/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.

[0096] 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.

[0097] 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.

[0098] 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.

[0099] 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_2S 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_2S concentration, additional samples would have been taken and the temperature maintained until two successive samples exhibited constancy in H_2S concentration.

[00100] 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

[00101] The following are enumerated embodiments which are provided as non-limiting examples:

[00102] A first embodiment, which is a process for activating and maintaining a catalyst for use in hydrotreating a hydrocarbon stream to simultaneously reduce heavier boiling components, chlorides, and olefins, comprising:

continuously contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen, wherein the hydrocarbon stream comprises one or more chloride compounds and one or more sulphides.

[00103] A second embodiment, which is the process of the first embodiment, wherein the one or more sulphides comprise dimethyl disulphide, mercaptans, carbon disulphide, hydrogen sulphide, or combinations thereof.

[00104] A third embodiment, which is the process of any one of the first through the second embodiments, wherein the one or more sulfides 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 a total weight of the hydrocarbon stream.

[00105] A fourth embodiment, which is the process of any of the first through the third embodiments, wherein the one or more sulfides of the hydrocarbon stream are present in an amount such that a sulphur content of the hydrocarbon stream is about 2 wt% based on a total weight of the hydrocarbon stream.

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

before the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst in the presence of hydrogen, contacting a catalyst activating stream with the hydroprocessing catalyst, wherein the catalyst activating stream comprises one or more sulphides.

[00107] A sixth embodiment, which is the process of the fifth embodiment, wherein the catalyst activating stream further comprises one or more hydrocarbons.

[00108] A seventh embodiment, which is the process of the sixth embodiment, wherein the one or more hydrocarbons comprise hexadecane.

[00109] An eighth embodiment, which is the process of any one of the fifth through the seventh embodiments, wherein the one or more sulfides of the catalyst activating stream are present in an amount such that a sulphur content of the catalyst activating stream is about 0.5 wt% to about 5 wt% based on a total weight of the catalyst activating stream.

[00110] A ninth embodiment, which is the process of any one of fifth through the eighth embodiments, wherein the one or more sulfides of the catalyst activating stream are present in an amount such that a sulphur content of the catalyst activating stream is about 3 wt% based on a total weight of the catalyst activating stream.

[00111] A tenth embodiment, which is the process of any one of the fifth through the ninth embodiments, wherein after the step of contacting and during the step of continuously contacting, the hydroprocessing catalyst has hydrogenation sites and hydrocracking sites.

[00112] An eleventh embodiment, which is the process of any one of the fifth through the tenth embodiments, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed for a period of 30 hours or less, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst initiates after the period elapses.

[00113] A twelfth embodiment, which is the process of any one of the fifth through the eleventh embodiments, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed ex-situ of a hydroprocessing reactor.

[00114] A thirteenth embodiment, which is the process of any one of the first and the twelfth embodiments, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst is performed ex-situ of the hydroprocessing reactor.

[00115] A fourteenth embodiment, which is the process of any one of the fifth through the thirteenth embodiments, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed in-situ of a hydroprocessing reactor.

[00116] A fifteenth embodiment, which is the process of any one of the first and the fourteenth embodiments, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst is performed in-situ of the hydroprocessing reactor.

[00117] A sixteenth embodiment, which is the process of any one of the first through the fifteenth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a temperature of 100 °C to 450 °C.

[00118] A seventeenth embodiment, which is the process of any one of the first through the sixteenth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a temperature of 100 °C to 350 °C.

[00119] An eighteenth embodiment, which is the process of any one of the first through the seventeenth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a temperature of 260 °C to 350 °C.

[00120] A nineteenth embodiment, which is the process of any one of the first through the eighteenth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a weight hourly space velocity of 0.1 to 10 hr^{-1}.

[00121] A twentieth embodiment, which is the process of any one of the first through the nineteenth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a hydrogen to hydrocarbon ratio of 10 to 3,000 NL/L.

[00122] A twenty-first embodiment, which is the process of any one of the first through the twentieth embodiments, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a pressure of 1 to 200 barg.

[00123] A twenty-second embodiment, which is the process of any one of the first through the twenty-first embodiments, wherein the hydrocarbon stream comprises the one or more chloride compounds in a concentration of greater than 200 ppmw based on a total weight of the hydrocarbon stream.

[00124] A twenty-third embodiment, which is the process of any one of the first through the twenty-second embodiments, wherein the hydrocarbon stream further comprises one or more olefins.

[00125] A twenty-fourth embodiment, which is the process of the twenty-third 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.

[00126] A twenty-fifth embodiment, which is the process of any one of the twenty-third through the twenty-fourth embodiments, wherein the hydrocarbon stream further comprises heavy hydrocarbon molecules, wherein the at least a portion of the one or more olefins comprises at least a portion of the heavy hydrocarbon molecules.

[00127] A twenty-sixth embodiment, which is the process of any one of the first or the twenty-third embodiment, wherein the hydrocarbon stream further comprises paraffins.

[00128] A twenty-seventh embodiment, which is the process of the twenty-sixth embodiment, wherein the hydrocarbon stream further comprises heavy hydrocarbon molecules, wherein the at least a portion of the one or more paraffins comprises at least a portion of the heavy hydrocarbon molecules.

[00129] A twenty-eighth embodiment, which is the process of any one of the first through the twenty-seventh embodiments, wherein the hydrocarbon stream further comprises heavy hydrocarbon molecules.

[00130] A twenty-ninth embodiment, which is the process of the twenty-eighth embodiment, wherein a concentration of the heavy hydrocarbon molecules in the hydrocarbon stream is 10 wt% to 90 wt% based on the total weight of the hydrocarbon stream.

[00131] A thirtieth embodiment, which is the process of any of the twenty-fifth and twenty-seventh through the twenty-ninth embodiments, wherein the heavy hydrocarbon molecules comprise C_{16} and larger hydrocarbons.

[00132] A thirty-first embodiment, which is the process of the thirtieth embodiment, wherein the C_{16} and larger hydrocarbons comprise paraffins, i-paraffins, olefins, naphthenes, aromatic compounds, or combinations thereof.

[00133] A thirty-second embodiment, which is the process of any one of the first through the thirty-first embodiments, wherein the hydrocarbon stream is one or more of a plastic pyrolysis oil and a tire pyrolysis oil.

[00134] A thirty-third embodiment, which is the process of any one of the first through the thirty-second embodiments, wherein the hydroprocessing catalyst comprises cobalt and molybdenum on an alumina support, nickel and molybdenum on an alumina support, tungsten and molybdenum on an alumina support, or nickel and molybdenum sulphides.

[00135] A thirty-fourth embodiment, which is the process of any one of the first through the thirty-third embodiments, wherein the hydroprocessing catalyst comprises platinum and palladium on an alumina support.

[00136] 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.

[00137] 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 activating and maintaining a catalyst for use in hydrotreating a hydrocarbon stream to simultaneously reduce heavier boiling components, chlorides, and olefins, comprising:

continuously contacting the hydrocarbon stream with a hydroprocessing catalyst in the presence of hydrogen, wherein the hydrocarbon stream comprises one or more chloride compounds and one or more sulphides.

2. The process of claim 1, wherein the one or more sulphides comprise dimethyl disulphide, mercaptans, carbon disulphide, hydrogen sulphide, or combinations thereof.

3. The process of claim 1, wherein the one or more sulfides 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 a total weight of the hydrocarbon stream.

4. The process of claim 1, further comprising:

before the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst in the presence of hydrogen, contacting a catalyst activating stream with the hydroprocessing catalyst, wherein the catalyst activating stream comprises one or more sulphides.

5. The process of claim 4, wherein the one or more sulfides of the catalyst activating stream are present in an amount such that a sulphur content of the catalyst activating stream is about 0.5 wt% to about 5 wt% based on a total weight of the catalyst activating stream.

6. The process of claim 4, wherein after the step of contacting and during the step of continuously contacting, the hydroprocessing catalyst has hydrogenation sites and hydrocracking sites.

7. The process of claim 4, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed for a period of 30 hours or less, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst initiates after the period elapses.

8. The process of claim 4, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed ex-situ of a hydroprocessing reactor.

9. The process of claims 1 and 8, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst is performed ex-situ of the hydroprocessing reactor.

10. The process of claim 4, wherein the step of contacting a catalyst activating stream with the hydroprocessing catalyst is performed in-situ of a hydroprocessing reactor.

11. The process of claims 1 and 10, wherein the step of continuously contacting a hydrocarbon stream with a hydroprocessing catalyst is performed in-situ of the hydroprocessing reactor.

12. The process of claim 1, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst is performed at a temperature of 100 °C to 450 °C.

13. The process of claim 1, wherein the step of continuously contacting the hydrocarbon stream with the hydroprocessing catalyst 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.

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

15. The process of claim 1, wherein the hydrocarbon stream further comprises one or more olefins, and 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.

16. The process of claim 15, wherein the hydrocarbon stream further comprises heavy hydrocarbon molecules, wherein the at least a portion of the one or more olefins comprises at least a portion of the heavy hydrocarbon molecules.

17. The process of claim 1 or 15, wherein the hydrocarbon stream further comprises paraffins.

18. The process of claim 1, wherein the hydrocarbon stream further comprises heavy hydrocarbon molecules, and wherein a concentration of the heavy hydrocarbon molecules in the hydrocarbon stream is 10 wt% to 90 wt% based on the total weight of the hydrocarbon stream.

19. The process of claim 1, wherein the hydroprocessing catalyst comprises cobalt and molybdenum on an alumina support, nickel and molybdenum on an alumina support, tungsten and molybdenum on an alumina support, or nickel and molybdenum sulphides.

20. The process of claim 1, wherein the hydroprocessing catalyst comprises platinum and palladium on an alumina support.

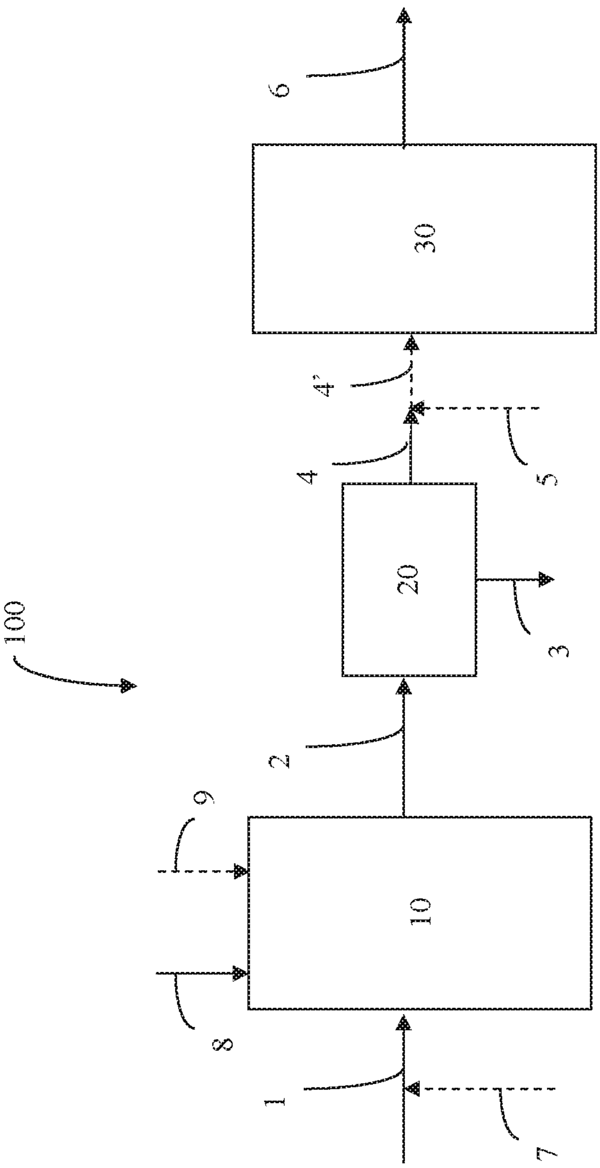
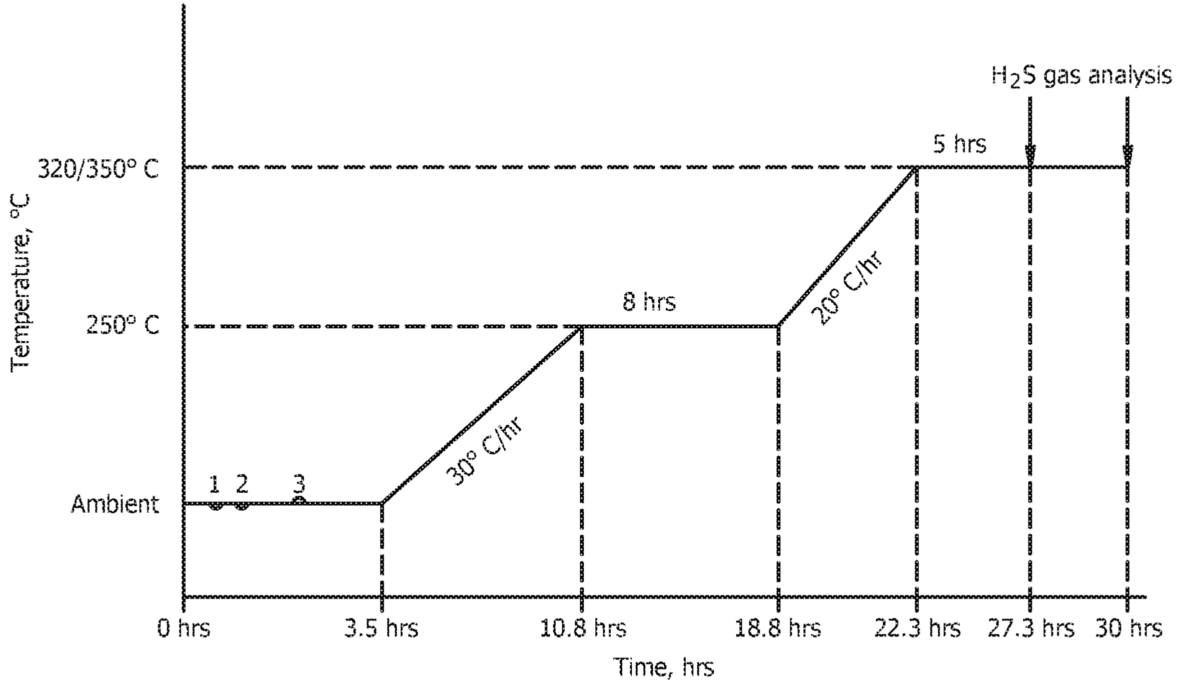


FIG. 1



1. H_2 purge for 30-60 mins at 40-60 barg at ambient temperature
2. Stop H_2
3. Pump sulfiding feed for 3hrs at $3 hr^{-1}$ WHSV without H_2 purge at 40-60 barg at ambient temperature

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051135

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/20 C10G1/10 C10G45/08 C10G45/10 C10G47/14
C10G49/04 C10G49/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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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

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"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

"&" document member of the same patent family

Date of the actual completion of the international search
10 May 2016

Date of mailing of the international search report
23/05/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051135

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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