

HYDROCARBON PYROLYSIS OF ADVANTAGED FEEDS

FIELD

[0001] The present disclosure relates to hydrocarbon pyrolysis of advantaged feeds, such as hydrocarbon feeds comprising at least one halogen-containing composition and at least one metal-containing composition. The present disclosure also relates to processes, methods, systems, and apparatus for upgrading the advantaged feeds; to processes, methods, systems, and apparatus for carrying out the pyrolysis; to the products of such pyrolysis; and to petrochemicals and polymers produced from such pyrolysis products.

BACKGROUND

10 [0002] Pyrolysis processes such as steam cracking produce useful products such as light olefin from feeds comprising hydrocarbon (“hydrocarbon feeds”), which are typically supplied in the liquid phase, vapor phase, or a mixture of liquid phase and vapor phase. A primarily liquid-phase hydrocarbon feed may be obtained via conduits from other refining or petrochemical facilities, pipeline, transport vessels, tankage, etc. For example, certain
15 primarily liquid-phase hydrocarbon feeds have been obtained raw sources, such as crude oil, and from various refinery process streams, e.g., naphtha, gas oil, medium-weight hydrocarbon (“medium hydrocarbon”), and heavy-weight hydrocarbon (“heavy hydrocarbon”), etc.

[0003] Recently, an increased demand for primarily liquid-phase hydrocarbon feeds has increased interest in utilizing relatively heavy liquid-phase feeds, e.g., those primarily liquid-phase hydrocarbon feeds that comprise one or more contaminants and have an API gravity less than or equal to that of naphtha (referred to as “advantaged feeds”). Although advantaged feeds can include those (e.g., certain gas oils) that have been subjected to prior processing, advantaged feeds also include those comprising raw feeds, such as crude oils comprising medium hydrocarbon and/or heavy hydrocarbon. For example, utilizing advantaged feeds
20 comprising raw feeds, e.g., various crude oils, would increase the supply of available liquid feeds, and would decrease the steam cracker facility’s dependence on refinery cuts to satisfy steam cracking feed needs. This in turn would improve facility economics, e.g., by decreasing light olefin production costs, and by making relatively high-value refinery cuts available for other purposes.

30 [0004] Contaminant management has been an obstacle to utilizing advantaged feeds for steam cracking, particularly in meeting increasingly stringent operating conditions and product specifications. Contaminants in certain advantaged feeds, e.g., those comprising gas oils, medium hydrocarbon, heavy hydrocarbon, and/or raw feeds (especially raw feeds comprising

one or more crude oils), may include one or more of particulates; asphaltenes; salts and other halogen-containing compositions, e.g., as chloride-containing compositions (“CCC”); metal and metal-containing compositions, e.g., nickel-containing compositions (“NCC”), and vanadium-containing compositions (“VCC”); among many others.

5 [0005] Processing difficulties arising from the presence of one or more of these contaminant compositions include (i) furnace coking, e.g., as can result from contaminants such as halogen-containing compositions (including salts), particulates, and asphaltenes; (ii) erosion and/or corrosion e.g., as can result from CCC contaminants and vanadium oxides produced during decoking mode; and (iii) deviations from product and byproduct
10 specifications, such as product specifications for pyrolysis gasoline. The utilization of advantaged feeds is also hindered by operational management difficulties, e.g., worsened catalyst performance during hydroprocessing of certain steam cracker product and co-product streams containing NCC and VCC (both poisons for many hydroprocessing catalysts); costs and operational interruptions arising from more-frequent steam cracking furnace decoking; the
15 cost of replacing or upgrading existing steam cracker equipment with corrosion-resistant alternatives made from more expensive materials, etc.

[0006] Thus there is a need for improved pyrolysis systems, apparatus, and processes that are capable of using a wider range of feeds, e.g., raw feeds, e.g., advantaged feeds, while substantially maintaining yields of desired products such as light olefin. More particularly,
20 there is a need for improved systems, apparatus, and processes for removing from advantaged feeds such contaminants as may otherwise cause coke formation, corrosion, product or co-product downgrading, and operational management difficulties during steam cracking.

SUMMARY

[0007] The invention is based in part on the development of processes, methods, systems, and apparatus for the hydrocarbon pyrolysis of advantaged feeds, such as those comprising
25 hydrocarbon and one or more of halogen-containing contaminants (e.g., chloride-containing contaminants), and metal-containing contaminants (e.g., one or more of nickel-containing contaminants and vanadium-containing contaminants).

[0008] In certain aspects, a hydrocarbon feed is an advantaged feed, e.g., a hydrocarbon
30 feed comprising hydrocarbon, a first composition comprising halogen, and a substantially different second composition comprising metal. It has been discovered desalting removes at least a portion of the hydrocarbon feed’s halogen-containing compositions, to produce a desalted feed. Typically, a portion of the hydrocarbon feed’s metal is in the form of one or

more salts, and a majority of these salts are typically removed during the desalting. An appreciable amount of other forms of metal, e.g., VCC and NCC, can be carried over into the desalted feed. In other words, the desalted feed can comprise at least a portion of the hydrocarbon feed's hydrocarbon and at least a portion of the hydrocarbon feed's metal-containing compositions, e.g., at least a portion of the hydrocarbon feed's NCC and/or at least a portion of the hydrocarbon feed's VCC. The desalted feed is preheated to form a preheated feed. When the pyrolysis is steam cracking, the preheating can be carried out in one or more convection coils located in a convection section of a steam cracking furnace. The preheated feeds can be combined with steam to produce a steam cracking feed, from which is separated a pyrolysis feed and a second stream. The separation transfers a portion of the steam cracking feed's metal-containing compositions to the second stream. The pyrolysis feed contains a lesser amount of the metal-containing compositions (on a weight percent basis) than does the second stream. At least a portion of the pyrolysis feed is pyrolysed to produce a pyrolysis effluent comprising at least a portion of the pyrolysis feed's metal-containing compositions. A bottoms stream and an upgraded pyrolysis effluent are separated from the pyrolysis effluent, wherein the upgraded pyrolysis effluent comprises light olefin. The separation transfers to the bottoms stream at least a portion of the pyrolysis effluent's metal-containing compositions.

BRIEF DESCRIPTION OF THE DRAWING

[0009] So that the manner in which the above recited features of the disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to implementations, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate certain implementations of this disclosure only, and are therefore not to be considered limiting of scope, for the disclosure may admit to other equally effective implementations.

[0010] FIG. 1 is a flow diagram of an embodiment of steam cracking and fractionating a hydrocarbon feed.

[0011] FIG. 2 is a flow diagram of an embodiment of pyrolysis gasoline and water separation and purification process.

[0012] FIG. 3 is a flow diagram of an embodiment of a light hydrocarbon recovery process.

[0013] To facilitate understanding, identical reference numerals have been used, where possible, to designate elements that are common to the Drawings and have similar function

and/or form. It is contemplated that elements and features of one implementation may be beneficially incorporated in other implementations without further recitation.

DETAILED DESCRIPTION

5 [0014] For the purpose of this description and appended claims, the following terms are defined:

Definitions

[0015] “Hydrocarbon” means a class of compounds containing hydrogen bound to carbon. The term “C_n” hydrocarbon means hydrocarbon having n carbon atom(s) per molecule, where n is a positive integer. The term “C_{n+}” hydrocarbon means hydrocarbon having at least
10 n carbon atom(s) per molecule, where n is a positive integer. The term “C_{n-}” hydrocarbon means hydrocarbon having no more than n number of carbon atom(s) per molecule, where n is a positive integer. “Hydrocarbon” encompasses (i) saturated hydrocarbon, (ii) unsaturated hydrocarbon, and (iii) mixtures of hydrocarbons, including mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds
15 having different values of n.

[0016] “Heavy hydrocarbon” means a mixture comprising hydrocarbon, the mixture having an API gravity in the range of from 5° up to (but not including) 22°. “Medium hydrocarbon” means a mixture comprising hydrocarbon, the mixture having an API gravity in the range of from 22° to 30°. A “relatively-heavy” hydrocarbon has an API gravity that is less
20 than that of naphtha.

[0017] The term “unsaturate” or “unsaturated hydrocarbon” means a C₂₊ hydrocarbon containing at least one carbon atom directly bound to another carbon atom by a double or triple bond. The term “olefin” means an unsaturated hydrocarbon containing at least one carbon atom directly bound to another carbon atom by a double bond. In other words, an olefin is a
25 compound which contains at least one pair of carbon atoms directly linked by a double bond. “Light olefin” means C₅₋ olefinic hydrocarbon.

[0018] “Primarily liquid phase” means a composition of which ≥ 50 wt. % is in the liquid phase, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %. A hydrocarbon feed is a primarily liquid-phase hydrocarbon feed when ≥ 50 wt. % of the hydrocarbon feed is in the liquid phase at a
30 temperature of 25°C and a pressure of 1 bar e.g., ≥ 75 wt. %, such as ≥ 90 wt. %.

[0019] “Raw” feed, e.g., raw hydrocarbon feed, means a primarily liquid-phase feed that comprises ≥ 25 wt. % of crude oil that has not been subjected to prior desalting and/or prior fractionation with reflux, e.g., ≥ 50 wt. %, such as ≥ 75 wt. %, or ≥ 90 wt. %.

[0020] Crude oil” means a mixture comprising naturally-occurring hydrocarbon of geological origin, where the mixture (i) comprises ≥ 1 wt. % of resid, e.g., ≥ 5 wt. %, such as ≥ 10 wt. %, and (ii) has an API gravity $\leq 52^\circ$, e.g., $\leq 30^\circ$, such as $\leq 20^\circ$, or $\leq 10^\circ$, or $< 8^\circ$. The crude oil can be classified by API gravity, e.g., heavy crude oil has an API gravity in the range of from 5° up to (but not including) 22° .

[0021] Normal boiling point and normal boiling point ranges can be measured by gas chromatograph distillation according to the methods described in ASTM D-6352-98 or D2887, as extended by extrapolation for materials above 700°C . The term “ T_{50} ” means a temperature, determined according to a boiling point distribution, at which 50 weight percent of a particular sample has reached its boiling point. Likewise, “ T_{90} ”, “ T_{95} ” and “ T_{98} ” mean the temperature at which 90, 95, or 98 weight percent of a particular sample has reached its boiling point. Nominal final boiling point means the temperature at which 99.5 weight percent of a particular sample has reached its boiling point. Steam cracker naphtha (also called “pyrolysis gasoline” or for simplicity “naphtha”) is a mixture of C_{5+} hydrocarbons, e.g., $\text{C}_5\text{-C}_{10+}$ hydrocarbons, having an initial atmospheric boiling point of about 25°C to about 50°C and a final boiling point of about 220°C to about 265°C , as measured according to ASTM D2887-18. In some examples, the naphtha can have an initial atmospheric boiling point of about 33°C to about 43°C and a final atmospheric boiling point of about 234°C to about 244°C , as measured by ASTM D2887-18.

[0022] Certain medium and/or heavy hydrocarbons, e.g., certain raw hydrocarbon feeds, such as certain crude oils and crude oil mixtures contain one or more of asphaltenes, precursors of asphaltenes, and particulates. Asphaltenes are described in U.S. Patent No. 5,871,634, which is incorporated herein by reference in its entirety. Asphaltene content can be determined using ASTM D6560 – 17. Asphaltenes in the hydrocarbon can be in the liquid phase (e.g., a miscible liquid phase), and also in a solid and/or semi-solid phase (e.g., as a precipitate). Typically asphaltenes and asphaltene precursors are present in at least the resid portion of the crude oil, and may also be present in lower-boiling portions of the crude oil. “Resid” means an oleaginous mixture, typically contained in or derived from crude oil, the mixture having a normal boiling point range $\geq 1050^\circ\text{F}$ (566°C). Resid can include “non-volatile components”, meaning compositions (organic and/or inorganic) having a normal boiling point range $\geq 590^\circ\text{C}$. Non-volatile components may be further limited to components with a boiling point of about 760°C or greater. Non-volatile components may include coke precursors, which are moderately heavy and/or reactive molecules, such as multi-ring aromatic compounds, which can condense from the vapor phase and then form coke under the specified steam cracking conditions.

Medium and/or heavy hydrocarbons (particularly the resid portion thereof) may also contain particulates, meaning solids and/or semi-solids in particle form. Particulates may be organic and/or inorganic, and can include coke, ash, sand, precipitated salts, etc. Although precipitated asphaltenes may be solid or semi-solid, precipitated asphaltenes are considered to be in the class of asphaltenes, not in the class of particulates.

[0023] The invention relates to advantaged feeds, namely hydrocarbon feeds that comprise one or more contaminants and have an API gravity less than or equal to that of naphtha. Certain advantaged feeds, e.g., crude oils, resids, etc., contain (i) compositions comprising halogen and (ii) substantially different compositions comprising metal; and may optionally comprise asphaltenes. The compositions comprising halogen can comprise, e.g., salts of monovalent metal, such as NaCl, KBr, etc; and divalent metal such as CaCl₂. Total salt content can be determined in accordance with ASTM D6470 - 99(2015) and ASTM D3230 - 13(2018). Compositions comprising metal may be found in a variety of hydrocarbon feeds, e.g., in heavy hydrocarbon, medium hydrocarbon, and even certain naphtha boiling-range hydrocarbon. For example, compositions comprising metal can be found in raw hydrocarbon feeds such as in extra heavy crude oil, heavy crude oil, medium crude oil, etc., and in hydrocarbon feeds that have been subjected to prior processing, e.g., in atmospheric gas oil, vacuum gas oil, atmospheric resid, and vacuum resid. Compositions comprising metal, such as VCC and NCC, can be found in a variety of chemical forms, such as metal compounds or metal-organic complexes. For example, metals such as Ni and V can be in the form of metal bound to asphaltenes, as metalloporphyrins, and/or as metal included in non-porphyrin forms. The indicated forms of metal-containing compositions are substantially different from those forms of halogen-containing compositions comprising and metal and halogen, e.g., those halogen-containing compositions where metal is bound to halogen. Compositions comprising metal typically comprise ≤ 1 wt. % of compounds having metal directly bound to halogen, e.g., ≤ 0.1 wt. %, such as ≤ 0.01 wt. %.

[0024] The term “chloride-containing compositions” or “CCC” means compositions (e.g., compounds) containing a chlorine atom, including salts of chlorine and chlorine containing hydrocarbons, for example sodium chloride, calcium chloride, ammonium chloride, and organic chlorides. CCC are in the class of halogen-containing compositions.

[0025] The term “nickel-containing compositions” or “NCC” means compositions (e.g., compounds) containing nickel, including nickel salts and nickel-containing hydrocarbon compounds, for example nickel oxide, and organonickel compounds, such as nickel

etioporphyrin. NCC in the form of a salt wherein nickel is directly bound to halogen are included in the class of halogen-containing compositions. Other forms of nickel-containing compositions are included in the class of metal-containing compositions.

5 **[0026]** The term “vanadium-containing compositions” or “VCC” means compositions (e.g., compounds) containing vanadium, including vanadium salts and vanadium-containing hydrocarbon compounds, for example vanadium oxide, and organovanadium compounds, such as vanadium etioporphyrin. VCC in the form of a salt wherein vanadium is directly bound to halogen are included in the class of halogen-containing compositions. Other forms of vanadium-containing compositions are included in the class of metal-containing compositions.

10 **[0027]** The term “concentration” or “content” as used herein means the amount by weight of a particular material as may be contained in a particular composition. In other words, the concentration (or content) of a particular material (e.g., atom, ion, compound, alloy, aggregate, etc.) in a particular composition is the amount (by weight) of the indicated material in a given weight of the indicted composition. Accordingly, the concentration of halogen, chloride, 15 vanadium, nickel, asphaltene, particulate, VCC, NCC, etc. in a composition means the amount (e.g., in weight percent or in parts per million by weight [“wppm”]) of that material in the composition, based on the total weight of the composition. For example, the amount of vanadium in a hydrocarbon feed (e.g., vanadium content or vanadium concentration) is the weight of vanadium (as vanadium atoms) in all its various forms (as compounds, alloys, etc.) 20 in a given weight of hydrocarbon feed. Likewise, the amount of VCC in a hydrocarbon feed is the weight of VCC (all forms of VCC) in a given weight of hydrocarbon feed, and the amount of particulates in a hydrocarbon feed is the weight of particulates (all forms, including inorganic oxides, hydrocarbon aggregates, etc.) in a given weight of hydrocarbon feed. As used in this description and appended claims, the same meanings apply by analogy to nickel, NCC, halide, 25 etc.

[0028] Steam cracking is a form of pyrolysis. Steam cracking is carried out in a steam cracker plant having furnace and recovery facilities. The furnace facility includes at least one steam cracker, also referred to as a steam cracking furnace. During pyrolysis mode, a hydrocarbon feed (typically after preheating) is combined with steam to produce a steam 30 cracking feed. The steam cracking feed, or a pyrolysis feed derived therefrom, is thermally cracked in the steam cracking furnace under pyrolysis conditions to produce a steam cracker effluent. Certain products, e.g., light olefin, are separated from the steam cracker effluent (or streams derived therefrom) in the recovery section. Steam can be introduced into the

hydrocarbon feed for a variety of reasons, such as to decrease hydrocarbon partial pressure, to control residence time, and/or to decrease coke formation. In at least one embodiment, the steam may be superheated, such as in the convection section of the steam cracking furnace, and/or the steam may be sour or treated process steam. During decoking mode, a flow of a
5 decoking fluid such as steam and/or air is substituted for at least a portion of the steam cracking feed to remove at least a portion of any coke that accumulated in the steam cracking furnace during pyrolysis mode.

[0029] The term “steam cracker tar” (“SCT”) means (a) a mixture of hydrocarbons having one or more aromatic components and optionally (b) non-aromatic and/or non-
10 hydrocarbon molecules, the mixture being derived from hydrocarbon pyrolysis and having a $T_{90} \geq 290^{\circ}\text{C}$, e.g., $\geq 500^{\circ}\text{C}$, such as $\geq 600^{\circ}\text{C}$, or greater. In certain aspects, SCT is separated from quench (or partially quenched) steam cracker effluent in a separation vessel such as tar knock-out drum, primary fractionator, etc. SCT can include hydrocarbon molecules (including mixtures and aggregates thereof) having (i) one or more aromatic components and (ii) a
15 molecular weight of about C_{15} or greater of about 50 wt. % or greater (e.g., 75 wt. % or greater, such as 90 wt. % or greater), based on the weight of the SCT.

[0030] Certain aspects of the invention will now be described in more detail which relate to the steam cracking of hydrocarbon feeds containing one or more of resid, salts, CCC, and NCC. The invention is not limited to these aspects, and this description should not be
20 interpreted as excluding other aspects within the broader scope of the invention.

[0031] It has been observed that CCC may form hydrochloric acid and ammonium chloride in a steam cracker plant. VCC may form corrosive vanadium oxide when operating a steam cracking furnace in decoking mode, leading to erosion and/or corrosion. The presence of vanadium oxide in the steam cracking furnace during pyrolysis mode, particularly in the
25 radiant coils and/or convection coils, may result in corrosion and add to the expense of installing new equipment or upgrading to corrosion-resistant equipment. NCC may increase coking of the steam cracking furnace causing more frequent switching from pyrolysis mode to decoking mode, leading to a decrease in light olefin production. NCC and/or VCC may poison certain hydroprocessing catalysts as used in the recovery facility and elsewhere. To counter
30 this, measures are typically taken to decrease the amount of NCC and VCC in streams that are subjected to hydroprocessing, e.g., by utilizing one or more guard beds. For improved steam cracking and cost efficiencies, one or more of (e.g. each of) CCC, NCC, and VCC may be managed at levels lower than a few wppm before entering the steam cracking furnace.

Furthermore, downstream operation may require even lower levels of NCC and VCC so as to avoid poisoning the hydroprocessing catalysts.

[0032] In certain aspects, the hydrocarbon feed is primarily in the liquid-phase and comprises hydrocarbon, a first composition comprising halogen, and a substantially different second composition comprising metal. These and other aspects include desalting the hydrocarbon feed (e.g., in one or more desalters) to produce a desalted feed having fewer halogen-containing compounds. The desalted feed is introduced into one or more convection coils within the convection section of a steam cracking furnace to form a preheated feed, which is combined with steam to produce a steam cracking feed. A pyrolysis feed having a lesser metal content than that of the steam cracking feed is separated from the steam cracking feed, e.g., in one or more vapor-liquid separators. The pyrolysis feed is introduced into at least one inlet of one or more radiant coils located in the radiant section of the steam cracking furnace. Pyrolysis (steam cracking) of the pyrolysis feed is carried out in the radiant coil(s). A steam cracker effluent is conducted out of at least one outlet of the radiant coil(s). Following one or more stages of cooling (e.g., quenching), the steam cracker effluent is introduced into one or more separation stages to separate from the steam cracker effluent at least a first stream comprising steam cracker tar and a second stream comprising upgraded steam cracker effluent comprising light olefin. Additional separations are carried out in the steam cracking plant's recovery facility, e.g., to recover from the upgraded steam cracker effluent products such as light olefin, and coproducts such as pyrolysis gasoline.

[0033] Certain hydrocarbon feeds will now be described in more detail. The invention is not limited to these hydrocarbon feeds, and this description should not be interpreted as excluding other hydrocarbon feeds within the broader scope of the invention.

Hydrocarbon Feeds

[0034] In certain aspects, the hydrocarbon feed comprises heavy hydrocarbon, a first composition comprising halogen, and a substantially different second composition comprising metal. The heavy hydrocarbon can comprise, e.g. one or more raw feeds, such as one or more crude oils. The heavy hydrocarbon typically includes relatively-high molecular weight hydrocarbons, such as those which pyrolyse to produce a relatively large amount of steam cracker naphtha (pyrolysis gasoline), steam cracker gas oil (SCGO), and steam cracker tar during steam cracking. The heavy hydrocarbon may include one or more of resid (also known as residual oil, or residues), gas oils, crude oil, atmospheric pipestill bottoms, vacuum pipestill streams including bottoms, condensates, heavy non-virgin hydrocarbon streams from

refineries, vacuum gas oils, heavy gas oil, naphtha contaminated with crude, atmospheric residue, heavy residue, C₄/residue admixture, naphtha residue admixture, gas oil residue admixture, low sulfur waxy residue, atmospheric residue, and heavy residue. It may be advantageous to use a heavy hydrocarbon feed including economically advantaged, minimally processed heavy hydrocarbon streams containing non-volatile components and coke precursors. The hydrocarbon feed can have a nominal final boiling point of about 315°C or greater, such as about 400°C or greater, about 450°C or greater, or about 500°C or greater. Typically there is about 1 wt. % or more of heavy hydrocarbon present in the hydrocarbon feed. For example, the hydrocarbon feed can include about 1 wt. % or more of heavy hydrocarbon, based on the weight of the hydrocarbon feed, such as about 25 wt. % or more, about 50 wt. % or more, about 75 wt. % or more, about 90 wt. % or more, or about 99 wt. % or more.

[0035] In certain aspects, the hydrocarbon feed further comprises one or more relatively low molecular weight hydrocarbon (light hydrocarbon). Light hydrocarbon typically includes one or more of heating oil, jet fuel, diesel, kerosene, coker naphtha, hydrocrackate, reformate, raffinate reformate, distillate, naphtha boiling-range hydrocarbon, and substantially saturated hydrocarbon molecules having fewer than five carbon atoms, e.g., ethane, propane, and mixtures thereof. Although hydrocarbon feeds comprising light hydrocarbon typically produce a greater yield of C₂ unsaturates (ethylene and acetylene) than do those comprising heavy hydrocarbon, heavy hydrocarbon is of increasing interest due to lower costs and higher availability.

[0036] In certain aspects, the hydrocarbon feed includes a medium and/or heavy hydrocarbon that comprises one or more of asphaltene, asphaltene precursors, and particulates.

[0037] The hydrocarbon feed may include CCC in a chloride concentration (the first chloride concentration) measured by ASTM D4929 - 17. The first chloride concentration of the hydrocarbon feed can be about 1 wppm or more, for example the first chloride concentration may be from about 1 wppm to about 400wppm, or about 10 wppm to about 350 wppm. The hydrocarbon feed may include NCC in a first nickel concentration measured by ASTM D5708 - 15. The first nickel concentration of the hydrocarbon feed can be about 40 wppm or less, e.g., from about 0 wppm to about 35 wppm, or 1 wppm to 30 wppm. The hydrocarbon feed may include VCC in a first vanadium concentration measured by ASTM D5708 - 15. The first vanadium concentration of the hydrocarbon feed can be about 30 wppm or less, e.g., from about 0.1 wppm to about 25 wppm, or about 1 wppm to about 20 wppm.

[0038] One or more desalters can be used to remove certain contaminants as may be found in certain advantaged feeds, e.g., hydrocarbon feeds comprising heavy hydrocarbon.

Upgrading Hydrocarbon Feed in a Desalter

[0039] One or more desalters may be included to remove from the hydrocarbon feed at least a portion of any salt and/or any particulate matter. While acceptable salt and/or particulate matter concentration vary with furnace design and operating conditions, the addition of a desalter may be desired when CCC is greater than a few ppm by weight of the hydrocarbon feed. Surprisingly, the desalter is observed to remove not only salts, but also particulates. This in turn leads to not only a decrease in steam cracking furnace corrosion and/or erosion (e.g., from solids eroding control-valve internals), but also to a decrease in (i) fouling throughout the steam cracker plant and (ii) a decrease in catalyst-effectiveness loss, e.g., as would otherwise occur from catalyst coking, plugging, poisoning, etc.

[0040] The desalting can be carried out in one or more conventional desalter vessels such as a plurality of vessels in semi-continuous operation, such as with one vessel (typically a drum) in use and the other under maintenance, but the invention is not limited thereto. The vessels and related equipment in the apparatus and system can be configured in series, parallel, and/or series parallel. Optionally, at least one of the vessels can include a mud-wash functionality and/or a tri-line sampling functionality, and can further include auxiliary equipment such as one or more brine tanks.

[0041] Desalting includes combining a wash water (or fresh water, or deionized water) with a hydrocarbon feed (optionally after heating) to produce a water-in-oil emulsion. Optional phases including (i) an oleaginous phase derived from the hydrocarbon feed and an aqueous phase derived from the wash water, may also be present. A solids phase may be present too. The desalter operates in part by transferring to the emulsion at least a portion of any salt, brine and particulates in the hydrocarbon feed and/or oleaginous phase, especially particulates having an appreciable dipole moment, such as those comprising aromatic cores. The wash water may be derived from various sources, e.g., recycled and/or recirculated water from other units in the facility, such as sour water stripper bottoms, overhead condensate, boiler feed water, with and/or without clarification, purification, etc. Alternately, or in addition, wash water may be obtained from other sources, e.g., from surface water sources such as from a river, and/or or from geological water sources, such as from one or more wells. The concentration of various salts in water can be expressed in parts per thousand by weight (for simplicity, parts per thousand), and typically salt concentration is in the range of from that of

fresh water (less than 0.5 parts per thousand of sodium chloride), brackish water (0.5 to 30 parts per thousand of sodium chloride), or saline water (30 to 50 parts per thousand of sodium chloride) to that of brine (more than 50 parts per thousand of sodium chloride). Although deionized water may be used to favor exchange of salt from the crude into the aqueous solution, 5 de-ionized water is not normally required to desalt crude oil feeds. In certain aspects, however, deionized water may be mixed with recirculated water from the desalter to achieve a specific ionic content in either the water before emulsification or to achieve a specific ionic strength in the final emulsified product. Wash water rates are typically in a range of from about 5% to about 7% by volume of the total crude oil to be desalted, but may be higher or lower dependent 10 upon the crude oil source and quality. Those skilled in the art will appreciate that a variety of water sources may be combined as determined by cost requirements, supply, salt content of the water, salt content of the hydrocarbon feed, and other factors specific to the desalting conditions such as the size of the separator and the degree of desalting required.

[0042] During the separation phase of a desalting process, the emulsion typically exhibits 15 a varying composition and thickness as desalting progresses. If unresolved, these emulsions may carry-over into the hydrocarbon feed and/or the oleaginous phase (the desalted feed) or carry-under into the aqueous phase. If carried-over, the emulsions may lead to coking or fouling of downstream equipment and disruption of the downstream fractionation process. If carried-under, they can disrupt the downstream water treatment process. Consequently, refiners 20 typically desire to either control the formation/growth of the emulsion or remove the emulsions from desalter units. It is also typical to utilize additional processing to resolve the emulsion into its constituent parts (i.e., to break the emulsion, resulting in separate oleaginous, aqueous, and solid phases). Doing so lessens difficulties associated with transferring the oleaginous phase (the desalted hydrocarbon feed), the aqueous phase, and the solids of the solids phase 25 away from the desalter.

[0043] As shown in FIG. 1, a salty emulsion is created by addition of wash water via line **103** to hydrocarbon feed **101** in desalter **105**. The hydrocarbon feed (comprising hydrocarbons, salts and other metal-containing material) and water are mixed and then separated producing (1) process water that is sent away via line **107** and (2) a desalted feed that is removed from 30 desalter **105** via line **109**.

[0044] Methods for separating from the emulsion the aqueous and oleaginous phases (and any solids present) and conducting these away from the desalter include gravitational and/or centrifugal methods. In a gravity method, density difference between the oleaginous and

the aqueous phases results in a separation of these phases by gravitational settling. In the centrifugation method, the emulsion is transferred from the desalter to a centrifuge (not shown) which separates the aqueous phase, oleaginous phase, and any solid from the emulsion. The gravity method generally requires the use of time-intensive, and thus inefficient, settling tanks as well as costly methods for disposing of the partially resolved emulsion, while the centrifugation method may require large centrifuges that are costly to build and operate.

[0045] Typically, an electric field is established in a region within the desalter to enhance water droplet coalescence. This in turn breaks the emulsion to form a typically-continuous oleaginous phase and a typically-continuous aqueous phase. Even when a relatively strong electric field is established in the desalter, the emulsion layer (also called a “rag layer”) may form, typically below the region in which the electric field is established. This emulsion layer is observed to be stable, even when adjacent to the strong electric field. The strength of this emulsion layer (sometimes called a “persistent emulsion”, indicating its resistance to emulsion-breaking) typically depends on factors such as hydrocarbon feed API gravity, the presence and amount of solids and semi-solids, such as particles, etc. Conventional methods for managing the rag layer can be used, but the invention is not limited thereto. For example, introducing into the desalter one or more de-emulsifier compositions and/or separating and conducting away at least a portion of the emulsion.

[0046] Certain hydrocarbon feed contaminants, including natural surfactants (asphaltenes and resins) and finely divided solid particles (e.g., less than 5 microns), stabilize the emulsion phase and cause the emulsion to persist in the desalter unit. The persistent emulsion problem is prevalent in the processing of hydrocarbon feeds comprising heavy hydrocarbon (such as crude oil) resulting from (it is believed) a relatively large solids content. Excessive solids content in the hydrocarbon feed (e.g., ≥ 10 ppmw of solids having a particle sizes < 5 microns), have been observed to stabilize the emulsion, leading to a progressive increase in rag layer thickness. While not wishing to be bound by any theory or model, it is believed that the existence of a persistent rag layer may result from an inability of electrocoalesced droplets to break the oil/bulk-resolved-water interface. The aqueous phase contains salts transferred from the hydrocarbon feed.

[0047] The invention is compatible with the use of de-emulsifiers (“demulsifiers”) to decrease rag layer size (e.g., height, when the plane of the rag layer is substantially parallel to the surface of the earth) and persistence. Conventional demulsifiers, such as those described in US. Patent Publication 2016/0208176 (incorporated by reference herein) can be used, but

the invention is not limited thereto. Suitable demulsifiers may be one or more of: polyethyleneimines, polyamines, succinated polyamines, polyols, ethoxylated alcohol sulfates, long chain alcohol ethoxylates, long-chain alkyl sulfate salts, e.g. sodium salts of lauryl sulfates, epoxies, and di-epoxides (which may be ethoxylated and/or propoxylated). The addition of demulsifiers may be useful in the desalting of hydrocarbon feeds containing high levels of particulates or asphaltenes, which tend to stabilize the rag layer.

[0048] The desalted hydrocarbon (which comprises the oleaginous phase) forms an upper region in the desalter, which is continuously removed via line **109**. The aqueous phase (comprising resolved bulk water, e.g., from coalesced droplets) accumulates in a lower region of the desalter and is continuously removed as a process water stream via line **107** (FIG. 1) as desalted feed. The process water may be sent for deionization and recycling or used with or without further processing in other processes, e.g., those located nearby the steam cracker facility.

[0049] It is observed for a wide range of hydrocarbon feeds, e.g., a wide range of medium and/or heavy crude oils, that operating the desalter under the specified desalting conditions transfers to the aqueous phase (i) ≥ 25 wt. % of the hydrocarbon feed's calcium content, typically ≥ 35 wt. %, or ≥ 50 wt. %; (ii) ≥ 75 wt. % of the hydrocarbon feed's sodium content, typically ≥ 85 wt. %, or ≥ 90 wt. %; (iii) ≤ 10 wt. %, typically ≤ 1 wt. % of the hydrocarbon feed's iron content, (iv) ≤ 10 wt. % of the hydrocarbon feed's nickel content, typically ≤ 1 wt. %, (v) ≤ 10 wt. % of the hydrocarbon feed's vanadium content, typically ≤ 1 wt. %, (vi) ≥ 25 wt. % of hydrocarbon feed's particulates, typically ≥ 35 wt. %, or ≥ 50 wt. %, and (vii) ≤ 10 wt. % of hydrocarbon feed's asphaltenes, typically ≤ 1 wt. %. Typically ≥ 75 wt. % of the hydrocarbon feed's hydrocarbon content resides in the desalted feed, e.g., ≥ 80 wt. %, such as ≥ 90 wt. %, or ≥ 99 wt. %, or in a range of from 80 wt. % to 100 wt. % based on the weight of the hydrocarbon in the hydrocarbon feed. The desalted feed has a chloride concentration (the second chloride concentration) measured by ASTM D4929 - 17. The second chloride concentration of the hydrocarbon feed can be about 50 wppm or less, for example the second chloride concentration may be in a range of from about 0.1 wppm to about 50 wppm, or about 1 wppm to 40 wppm. In certain aspects, (i) the hydrocarbon feed comprises at least one heavy hydrocarbon, and (ii) the desalted feed has a halogen concentration CH_1 , the hydrocarbon feed has a halogen concentration CH_2 , and the mass ratio of CH_1 to CH_2 is in the range of from 0.01 : 1 to 0.5 : 1. Optionally, the desalted feed has a chloride concentration CC_1 , the hydrocarbon feed has a chloride concentration CC_2 , and the mass ratio of CC_1 to CC_2 is in the range of from

0.01 : 1 to 0.5 : 1. It is observed for a broad range of hydrocarbon feeds that what the desalted feed has an asphaltene concentration CA_1 , and the hydrocarbon feed has a asphaltene concentration CA_2 , and the mass ratio of CA_1 to CA_2 is in the range of from 0.9:1 to 1:1. Typically the desalting removes ≥ 25 wt. % of any particulates contained in the hydrocarbon feed, based on the weight of the hydrocarbon feed, e.g., ≥ 25 wt. %, such as ≥ 50 wt. %, or ≥ 75 wt. %, or ≥ 90 wt. %.

[0050] Certain aspects of the invention will now be described in more detail which include steam cracking a pyrolysis feed obtained from at least one vapor-liquid separator that is integrated with a steam cracking furnace convection section. The invention is not limited to these aspects. This description should not be interpreted as excluding other aspects within the broader scope of the invention, such as those that do not utilize a vapor-liquid separator integrated with the steam cracking furnace convection section.

Steam Cracker

[0051] Steam cracking is carried out in at least one steam cracking furnace that includes a radiant section having at least one tubular heat exchange member (a “radiant coil”) and a convection section that also has at least one tubular heat exchange member (a “convection coil”). The steam cracking furnace may have a flash separator integrated by fluid connection between the convection section and the radiant section. The radiant section can include fired heaters (burners), and flue gas from combustion carried out with the fired heaters travels upward from the radiant section through the convection section and then away as flue gas. As shown in FIG. 1, the desalted feed via line **109** first enters steam cracker **111** in the convection section (upper portion) and is sent through convection line **113** where it is preheated by indirect exposure to the flue gases in the convection section to produce a preheated feed. The preheated feed is typically combined with steam (not shown) and conducted via line **115** to flash separator **117**. At least bottoms stream (typically primarily-liquid phase) and a primarily-vapor phase pyrolysis feed are separated from the preheated feed. The bottoms stream (which typically comprises resid) is conducted away via line **119**. The pyrolysis feed is conducted to the radiant (lower) section of steam cracking furnace **111** (optionally after additional heating in the convection section) via line **121**. The pyrolysis feed is conducted through radiant line **123** for pyrolysis (cracking) to produce a steam cracking effluent that is transferred to line **125** for further processing.

Steam Cracker Convection Section

[0052] In these and other aspects, the desalted feed (via line 109) is preheated in the convection section of steam cracking furnace 111 to produce a preheated feed. The preheating of the desalted feed can be accomplished, for example, by passing the desalted feed through bank of heat exchange tubes (e.g., a plurality of convection coils) located within the convection section of the steam cracker. The preheating is typically carried out to achieve a temperature of the preheated feed in a range of from about 150°C to about 260°C, such as about 160°C to about 230°C, or about 170°C to about 220°C.

[0053] The amount of preheated feed that is in the liquid phase can be regulated to further decrease the amount of salt and/or particulate matter included in the steam cracking feed and pyrolysis feed. For example, process conditions (such as temperature and/or flow rate) in convection coils utilized for feed preheating can be regulated to increase the portion of preheated feed in the liquid phase to an amount of about 2% or greater, such as about 5% or greater, based on the total weight of hydrocarbon in the preheated feed. Doing so has been found to decrease the amount of salt and/or particulate matter included in the steam cracking feed and pyrolysis feed, it is believed by suspending a greater amount of these undesired contaminants in the liquid phase. Those skilled in the art will appreciate that the amount of preheated feed in the liquid phase that is needed to do this may vary with the quantity of salt and/or particulate matter in the hydrocarbon feed. For hydrocarbon feeds comprising more viscous, generally heavier, liquid phase hydrocarbons, a preheated feed having a lesser amount of liquid phase material is needed to suspend a greater amount of these undesired contaminants in the liquid phase. Alternatively or in addition, maintaining a sufficient velocity of liquid-phase material in the convection coils utilized for feed preheating has been found to keep at least a portion of the salt and/or particulate matter contained in the desalted feed suspended in the liquid-phase during feed preheating and the flash separation. Those skilled in the art will appreciate that a liquid fraction of greater mass may be required at a lesser flow stream velocity.

[0054] The preheated feed is typically combined with steam to produce a steam cracking feed, which is typically subjected to additional heating in a second bank of convection coils in the convection section. The steam cracking feed typically comprises steam in an amount in a range of from about 10 wt. % to about 90 wt. %, based on the weight of the steam cracking feed. In certain aspects, the steam cracking feed has a weight ratio of steam to preheated feed in the range of from about 0.1 to about 1, such as about 0.2 to about 0.6.

[0055] Aspects will now be described in more detail which include producing a pyrolysis feed by separating from the steam cracking feed in a flash separation at least (i) primarily vapor-

phase composition and (ii) a bottoms stream that typically is primarily liquid-phase. The invention is not limited to these aspects, and this description should not be interpreted as excluding other methods for producing the pyrolysis feed within the broader scope of the invention.

5 Flash Separation

[0056] In certain aspects, steam cracking furnace (**111**) is integrated with at least one flash separator **117**, which includes at least one a vapor/liquid separator (sometimes referred to as flash pot or flash drum). Such flash separators are typically advantageous when the preheated feed includes about 0.1 wt. % or more of asphaltenes based on the weight of the preheated feed, e.g., about 5 wt. % or more. The invention is compatible with conventional flash separators, e.g., those disclosed in U.S. Pat. Nos. 6,632,351; 7,138,047; 7,090,765; 7,097,758; 7,820,035; 7,311,746; 7,220,887; 7,244,871; 7,235,705; 7,247,765; 7,351,872; 7,297,833; 7,488,459; 7,312,371; and 7,578,929 (which are incorporated by reference herein), but the invention is not limited thereto.

15 [0057] The flash separator is integrated with the steam cracker to lessen the difficulties associated with separation a primarily vapor-phase pyrolysis feed from the steam cracking feed. In these and other aspects, the steam cracking feed (via line **115**) is transferred to and flashed in flash separator **117** to separate from the steam cracking feed at least (i) a bottoms stream that is typically primarily liquid-phase, and (ii) a primarily vapor-phase composition. At least a portion of the high molecular-weight compounds (and aggregates thereof), such as asphaltenes, in the steam cracking feed are transferred to the bottoms stream, which can be conducted away from flash separator **117** via line **119**. The bottoms stream may include, for example, greater than about 10 wt. % of the asphaltenes in the preheated hydrocarbon feed, typically ≥ 50 wt. %, such as ≥ 75 wt. %, or ≥ 90 wt. %, or ≥ 99 wt. %. The bottoms stream can comprise material that is not in the liquid phase, e.g., precipitated solids such as asphaltenes and solids disengaged from the steam cracking feed. The pyrolysis feed, comprising at least a portion of the primarily-vapor phase composition, is conducted to the steam cracker's radiant section via line **121** for pyrolysis.

[0058] An advantage of having a flash separator downstream of the convection section and upstream of the radiant section is an increased breadth of hydrocarbon sources available to be used directly, without pretreatment, as hydrocarbon feed **101**. For example, the addition of a flash separator downstream of convection line **113** allows for hydrocarbon feed **101** to contain about 50 wt. % or greater of raw feeds comprising crude oil (e.g., those comprising one or more

heavy and/or medium crude oils), such as about 75 wt. % or greater, or about 90 wt. % or greater.

5 **[0059]** The use of a flash separator upstream of the radiant section of the steam cracking furnace increases steam cracker operability and efficiency, even when steam cracking a steam cracking feed comprising undesired contaminants carried over from the preheated feed. As a result of this separation, the amount of contaminants in the primarily vapor-phase composition (and thus in the pyrolysis feed) may be kept within desired limits. A major amount (e.g., substantially all) of the steam cracking feed's salt and particulate matter is conducted away from a lower region of the flash separator via the bottoms stream.

10 **[0060]** The flash separator may operate at a temperature from about 315°C to about 510°C and/or a pressure from about 275 kPa to about 1400 kPa, such as, a temperature from about 430°C to about 480°C, and/or a pressure from about 700 kPa to about 760 kPa. In certain aspects, e.g., those where the raw feed's crude oil comprises heavy hydrocarbon, less than about 98% of the preheated feed is typically in the vapor phase at the inlet of the flash separator.

15 **[0061]** At least a portion of the flashed primarily vapor-phase composition is included in the pyrolysis feed. The pyrolysis feed can be subjected to additional heating in the steam cracking furnace's convection section downstream of the flash separation. The pyrolysis feed or heated pyrolysis feed (as the case may be) is then conducted (typically via cross-over piping) into at least one radiant coil for pyrolysis in the radiant section of the steam cracking furnace.

20 The bottoms stream from the steam cracking feed can be conducted away from the flash separator, e.g., for storage and/or further processing.

[0062] It is observed for a wide range of hydrocarbon feeds, e.g., a wide range of medium and/or heavy crude oils, that operating the flash separator under the specified flash separation conditions transfers to the flash separator's bottoms stream (i) ≥ 75 wt. % of the steam cracking feed's calcium content, typically ≥ 90 wt. %, or ≥ 98 wt. %; (ii) ≥ 75 wt. % of the steam cracking feed's sodium content, typically ≥ 90 wt. %, or ≥ 98 wt. %; (iii) ≥ 75 wt. % of the steam cracking feed's iron content, typically ≥ 90 wt. %, or ≥ 98 wt. %; (iv) ≥ 75 wt. % of the steam cracking feed's nickel content, typically ≥ 90 wt. %, or ≥ 98 wt. %; (v) ≥ 75 wt. % of the steam cracking feed's vanadium content, typically ≥ 90 wt. %, or ≥ 98 wt. %, (vi) ≥ 75 wt. % of the steam cracking feed's particulates, typically ≥ 90 wt. %, or ≥ 98 wt. %; and (vii) ≥ 75 wt. % of the steam cracking feed's asphaltenes, typically ≥ 90 wt. %, or ≥ 98 wt. %. Typically, ≥ 90 wt. % of any asphaltenes produced and/or precipitated during the flash separation are transferred to the bottoms stream, e.g., ≥ 99 wt. %. The pyrolysis feed has a chloride concentration (a third

chloride concentration), as measured by ASTM D4929 - 17. The third chloride concentration can be about 10 wppm or less, for example the third chloride concentration may be from about 0.01 wppm to about 10 wppm, or 1 wppm to 5 wppm. The pyrolysis feed has a nickel concentration (a second nickel concentration), as measured by ASTM D5708 – 15. The second nickel concentration can be about 5 wppm or less, for example the second nickel concentration may be from about 0.1 wppm to about 5 wppm, or 1 wppm to 4 wppm. The pyrolysis feed has a vanadium concentration (a second vanadium concentration), as measured by ASTM D5708 – 15. The second vanadium concentration can be about 5 wppm or less, for example the second vanadium concentration may be from 0.1 wppm to about 5 wppm, or 1 wppm to 4 wppm.

10 Steam Cracker Radiant Section

[0063] As shown in FIG. 1, a pyrolysis feed is introduced into at least one radiant coil **123**, where at least a portion of the hydrocarbon in the pyrolysis feed is pyrolysed to produce a steam cracker effluent comprising including C₂₊ olefins, particularly ethylene and propylene. The pyrolysis feed is typically in the vapor phase at the inlet of the radiant coils, e.g., about 90 wt. % or greater of the steam cracking feed is in the vapor phase, such as about 95 wt. % or greater, or about 99 wt. % or greater. Heat from combustion carried out by the burners is transferred through the walls of the radiant coils to indirectly heat the pyrolysis feed for the endothermic pyrolysis reaction. The steam cracker effluent is conducted away from the radiant coil via line **125**.

20 **[0064]** Steam cracking conditions (pyrolysis conditions) may include exposing the pyrolysis feed in the radiant coil **123** to a temperature (measured at the outlet of the radiant line) of about 400°C or greater, such as, from about 400°C to about 1100°C, and a pressure of about 10 kPa or greater, and a steam cracking residence time from about 0.01 second to 5 seconds. For example, the steam cracking conditions can include one or more of (i) a temperature of about 760°C or greater, such as from about 760°C to about 1100°C, or from about 790°C to about 880°C, or for hydrocarbon feeds containing light hydrocarbon from about 760°C to about 950°C; (ii) a pressure of about 50 kPa or greater, such from about 60 kPa to about 500 kPa, or from about 90 kPa to about 240 kPa; and/or (iii) a residence time from about 0.1 seconds to about 2 seconds. The steam cracking conditions may be sufficient to convert at least a portion of the steam cracking feed's hydrocarbon molecules to C₂₊ olefins by pyrolysis.

30 **[0065]** The steam cracker effluent generally includes unconverted pyrolysis feed and products of the pyrolysis ("pyrolysis products"). For example, the steam cracker effluent can include material contained in and/or derived from impurities and/or contaminants in the

pyrolysis feed, e.g. particulates, heteroatom compounds, etc. The pyrolysis products can include, e.g., C₂₊ hydrocarbon (saturated and unsaturated) and SCT. Typically, the pyrolysis products include molecular hydrogen, methane, C₂₊ olefin, acetylene, C₆₊ aromatic hydrocarbon, C₂₊ saturated hydrocarbon, C₃₊ diolefin, aldehydes, mercaptans, acidic gases
5 such as H₂S and/or CO₂, steam cracker tar and steam cracker tar precursors (including asphaltenes), coke, coke precursors, particulates (including coke particulates), etc. Those skilled in the art will appreciate that at least a portion of any impurities comprising various chemical and physical forms of metal and metal-containing compounds in the pyrolysis feed are typically converted to different forms by the pyrolysis.

10 **[0066]** After exiting the radiant coil, the steam cracker effluent is cooled (e.g., quenched), typically at a location proximate to the radiant coil's outlet. The quenching is carried out to rapidly achieve a steam cracker effluent temperature at which conversion to undesired products such as saturated light hydrocarbon, SCT, and coke is substantially attenuated. Conventional cooling and/or quenching equipment can be used, e.g., one or more transfer line exchangers,
15 quench headers, etc., but the invention is not limited thereto.

[0067] SCT is a high-boiling point, viscous, reactive material that can foul equipment under certain conditions. Steam cracker tar can form during the pyrolysis or the pyrolysis feed, and also can form in the steam cracker effluent—particularly before effluent quenching and/or cooling. In general, hydrocarbon feeds containing higher boiling materials tend to produce
20 greater quantities of SCT. In at least one embodiment, the steam cracker effluent is quenched by rapid cooling, e.g., in a quench header and/or through one or more heat exchangers (not shown in FIG. 1). Generally, the effluent leaving the first heat exchanger may remain at a temperature above the hydrocarbon dew point (the temperature corresponding to the onset of hydrocarbon condensation from the vapor phase) of the steam cracker effluent. For a typical
25 hydrocarbon feed containing heavy hydrocarbons under cracking conditions, the hydrocarbon dew point of the steam cracker effluent may be from about 375°C to about 650°C, such as from about 480°C to about 600°C. At temperatures greater than the hydrocarbon dew point, the fouling tendency is lessened, because vapor-phase fouling is generally not severe, and there is little to no liquid present that could cause fouling. The steam cracker effluent may be further
30 cooled, e.g., by one or more of additional heat exchangers, direct quench before reaching the tar knock-out drum, direct quench within the tar knock-out drum, etc.

[0068] In the aspects illustrated in FIG. 1, the steam cracker effluent is subjected to direct quench at a point between the outlet of radiant line **123** and the inlet of tar knock-out drum **127**.

The quench is accomplished by contacting the steam cracker effluent with one or more quench streams. This can be carried out in lieu of, or in addition to cooling carried out with one or more transfer line exchangers. Where employed in conjunction with at least one transfer line exchanger, a quench stream may be introduced at a point downstream of the transfer line exchanger(s). Suitable quench streams include oleaginous and/or aqueous streams. The quench stream can be a vapor-phase stream (e.g., steam), liquid-phase stream (e.g., quench oil) or a mixture having liquid and vapor phases. Conventional quench oils can be used, such as those obtained from one or more of a knock-out drum, SCT hydroprocessing facility, and primary fractionator, but the invention is not limited thereto.

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10 **[0069]** Certain aspects will now be described in more detail which include a tar knock-out drum for separating from the steam cracker effluent (i) a bottoms stream comprising SCT and (ii) an overhead stream comprising upgraded steam cracker effluent. The invention is not limited to these aspects, and this description should not be interpreted as excluding other forms of SCT separation and upgraded steam cracker effluent separation within the broader scope of the invention.

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Tar Knock Out Drum

[0070] The cooled and/or quenched steam cracker effluent is fed to at least one tar knock-out drum (a separation vessel), where a typically flow-able bottoms stream comprising SCT is separated from the steam cracker effluent. Those skilled in the art will appreciate that the separation should be carried out at a temperature that is less than or equal to that needed to condense ≥ 50 wt. % of SCT in the quenched and/or cooled steam cracker effluent out of the vapor phase, based on the weight of the SCT in quenched and/or cooled steam cracker effluent. Typically, ≥ 75 wt. % of SCT in the quenched and/or cooled steam cracker effluent is condensed out of the vapor phase, e.g., ≥ 90 wt. %, such as ≥ 95 wt. %, or ≥ 99 wt. %.

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25 **[0071]** Besides SCT, the bottoms stream can further comprise particulates (e.g., coke particles) and other contaminants contained in and/or derived from the pyrolysis feed. Typically, the cooled and/or quenched steam cracker effluent has a temperature $\leq 350^{\circ}\text{C}$ at the tar knock-out drum's inlet, such as in a range of from about 200°C to about 350°C , or from about 240°C to about 320°C . The separated SCT typically accumulates in a lower region of the tar knock-out drum, e.g., proximate or adjacent to an outlet location for conducting away the bottoms stream. The temperature of the cooled and/or quenched steam cracker effluent at the tar knock-out drum's inlet and the process conditions in the tar knock-out drum (and ancillary equipment such as pumps, valves, and coolers) are typically regulated to achieve an average

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temperature of separated SCT accumulated in the tar knock-out drum that is $\leq 175^{\circ}\text{C}$, e.g., $\leq 150^{\circ}\text{C}$. A minor amount of certain contaminants are typically found in mixed with the accumulated SCT. Among these contaminants are those carried over from the pyrolysis feed, those produced during the pyrolysis, and those formed in the tar knock-out drum. Various chemical and/or physical forms of one or more of iron, nickel, and vanadium can be included in the bottoms stream, e.g., as metallic particulates. Particles comprising one or more of iron, nickel, and vanadium also can be entrained in the overhead stream. Vaporized forms of iron, nickel, and vanadium can also be present in the overhead stream. Depending, e.g., on the temperature of the accumulated SCT and the time duration during which the accumulated SCT is maintained in the tar knock-out drum, additional particulates and the additional particulate precursors may form in the accumulated SCT. The additional particulates and additional particulate precursors (e.g., asphaltenes and precipitated asphaltenes) are typically conducted away with the bottoms stream, e.g., mixed with the SCT in the bottoms stream.

[0072] At least part of the quenching and/or cooling of the steam cracker effluent can be carried out within the tar knock-out drum, e.g., by contacting the steam cracker effluent with one or more of the specified quench streams. Quenching and/or cooling in the tar knock-out drum may be adjusted to lessen or substantially prevent the formation of asphaltenes, e.g., besides or in addition to that occurring between the radiant coil outlet and the tar knock-out drum. It is observed that quenching and/or cooling in the tar knock-out drum can appreciably decrease the weight of asphaltene formation in the tar knock out drum (“A₁”) in comparison with the weight of asphaltenes formed in a tar knock-out drum operating under substantially similar conditions but without quenching and/or cooling in the tar knock-out drum (“A₂”). For example, $[(A_2 - A_1) / A_2]$ can be ≤ 0.7 , e.g., ≤ 0.5 , such as ≤ 0.3 .

[0073] In the aspects illustrated in FIG. 1, tar knock-out drum **127**, accepts quenched and/or cooled steam cracker effluent (via line **125**) and separates therefrom a bottoms stream comprising SCT (which is transferred to line **129**) and an overhead stream comprising upgraded steam cracker effluent (which is transferred to line **139**). Conventional tar knock-out drums can be used, but the invention is not limited thereto. For example, the tar knockout drum can have the form of an empty vessel, lacking distillation plates or stages, but having at least one inlet adapted for admitting the quenched and/or cooled steam cracker effluent, and at least two outlets: one adapted for conducting away the bottoms stream and another adapted for conducting away the overhead stream. If desired, multiple knock-out drums may be connected in parallel such that individual drums can be taken out of service and cleaned while the plant

is operating. Typically, the bottoms stream exiting the tar knock-out drum has an initial boiling point $\geq 150^{\circ}\text{C}$, e.g., $\geq 200^{\circ}\text{C}$, such as an initial boiling point in the range of from about 150°C to about 320°C .

5 [0074] In at least one embodiment, a purge stream (not shown in FIG. 1) is introduced to the tar knock-out drum to decrease liquid-vapor contact. Typically, the purge stream is selected from steam, inert gas such as nitrogen, and substantially non-condensable hydrocarbons, such as those obtained from steam cracking, examples of which include cracked gas and tail gas. Purge gas, when used, can be conducted away as part of the overhead stream, i.e., together with the upgraded steam cracker effluent.

10 [0075] At least a portion of the bottoms stream conducted away from the tar knock-out drum can be used as a quench stream, e.g., in the tar knock-out drum and/or at one or more locations that are both upstream thereof and downstream of the radiant coil outlet. Such a quench stream can be produced, e.g., by cooling the at least a portion of the bottoms stream and/or by cooling SCT recovered from the tar knock-out drum's bottoms stream. Conventional
15 cooling equipment and methods can be used, but the invention is not limited thereto, e.g., one or more shell-and-tube exchanger, spiral wound exchanger, airfin, or double-pipe exchangers, etc. In at least one embodiment, the bottoms stream is cooled from a temperature of about 280°C to about 150°C . In another embodiment, the cooled bottoms stream is recycled and is introduced to the separation vessel. The amount of cooling and the amount of recycle are
20 regulated to achieve an average temperature of the accumulated (separated) SCT within the tar knock-out drum of about 175°C or less, such as about 150°C or less.

[0076] An appreciable reduction in the rate of asphaltene and SCT formation in line 125 and tar knock-out pot 127 is observed when the cooled bottoms stream is recycled as a quench stream to a location downstream of the radiant coil outlet. Surprisingly, doing so also results
25 in a viscosity decrease in the tar knock-out drum bottoms stream at the tar knock-out drum's outlet. This in turn results in a bottoms stream that may meet fuel oil viscosity specifications (e.g., those applicable to marine fuel oil), even in the absence or reduction of an added externally sourced light (e.g., lower-viscosity) blend stock that would otherwise be needed in the absence of such recycling.

30 [0077] Typically, the bottoms stream comprising the SCT is conducted away for further processing, e.g., in a clean fuels unit to produce an upgraded SCT, e.g., a hydroprocessed SCT. Likewise, the overhead stream comprising the upgraded steam cracker effluent typically is conducted away for further processing, e.g., to recover and conduct away a primarily vapor-

phase process gas comprising ethylene and/or propylene. Process gas is typically recovered in a separation apparatus, e.g., in one or more primary fractionators, one or more quench towers, and/or combinations of quench towers and primary fractionators. Aspects utilizing a combination primary fractionator-quench tower will now be described in more detail. The invention is not limited to these, and this description should not be interpreted as excluding other forms of process gas separation and recovery within the broader scope of the invention.

Primary Fractionator

[0078] In certain aspects, an overhead stream comprising upgraded steam cracker effluent is conducted via line **139** to primary fractionator **141** and quench tower **147**, for separation from the upgraded steam cracker effluent of a process gas, a substantially flow-able bottoms stream, and at least two side stream. Stream 139 is introduced into the primary fractionator flash zone so that the vapor goes to the trays above and any liquid goes to the tower bottom. As shown in FIG. 1, the flow-able bottoms stream conducted away via line **143** can be divided, with a first part being returned to the combination primary fractionator-quench tower (for simplicity, the combination is referred to herein as a “PF-QT”) and a second part being utilized as a quench oil for quenching steam cracker effluent exiting the radiant coil. Although FIG. 1 shows the first part of the flow-able bottoms returned to the PF-QT in combination with the upgraded steam cracker effluent, this is not required. For example, the first part (and/or additional parts) of the flow-able bottoms can be recycled to the PF-QT at any suitable location for maintaining the desired PF-QT separation conditions, e.g., via a pump-around loop with optional direct or indirect heating and/or cooling. A stream comprising steam cracked gas oil (“SCGO”) is conducted away from the PF-QT via line **145**, the SCGO typically including about 90 wt. % or greater of C₁₀ - C₁₇ hydrocarbon based on the weight of the SCGO. The SCGO typically has a T₉₀ boiling point in the range of from about 160°C to about 290°C. A side stream comprising steam cracker naphtha (“SCN”; or pyrolysis gasoline, “pygas”) is conducted away from the PF-QT via line **149**. The SCN typically includes C₅ - C₁₀ hydrocarbon. The process gas is conducted away from the PF-QT via line **151**. One or more of ethylene, propylene, normal butenes, and isobutene recovered and removed from the process gas can be recovered and polymerized, e.g., to produce polymers having units derived from one or more of the ethylene, propylene, normal butenes, and isobutene. Such polymers include one or more of polyethylene, polypropylene, ethylene-propylene copolymer, polymers and/or copolymers of C₄ olefins and/or isoolefin such as butyl rubber, etc. At least a portion of the

separated and recovered C₃₊ olefin can be converted to oxygenates such as MTBE and/or alkylated to produce, e.g., one or more of diisobutene, isooctene, isooctane, etc.

[0079] The flow-able bottoms conducted away from the PF-QT via line **143**. The flow-able-bottoms typically comprises viscous heavy hydrocarbon. The viscosity of this stream can be controlled by the addition of a light blend stock, which may be introduced directly to the lower region of the PF-QT (e.g., at a location proximate to or adjacent to the outlet for line **143**). Doing so can also cool or heat the flow-able bottoms to achieve a desired temperature, e.g. before returning the recycle portion of the flow-able bottoms stream to the PF-QT. Alternately or in addition, the light blend stock may be added downstream of the primary fractionator, e.g., introduced directly into that part of the flow-able bottoms stream that will be recycled to the PF-QT. Such light blend stocks may include, e.g., one or more of SCGO, distillate quench oil and cycle oil, such as cycle oil obtained from a fluidized catalytic cracking unit,. When used, the light blend stock can have a viscosity at a temperature of 93°C of about 1,000 centistokes (cSt) or less, such as about 500 cSt or less, or about 100 cSt or less.

[0080] A primarily vapor-phase composition is disengaged from liquid in the primary fractionator, and is passed through the overhead of the primary fractionator into a quench tower (such as quench tower **147**). In quench tower **147**, the vapor-phase composition is rapidly cooled (quenched) as it passes through water (vapor or liquid). The water can be obtained from a variety of sources, for example, recycled refinery water, recirculated wastewater, clarified fresh water, purified wastewater, sour water stripper bottoms, overhead condensate, boiler feed water, or from other water sources or combinations of water sources. Water is commonly recycled from downstream oil water separators, sour water separators, and pygas strippers. The quench tower condenses at least a portion of pygas present in the vapor-phase composition. Condensed pygas and heated quench water are withdrawn from a location proximate to the bottom of the quench tower as the pygas stream **149**.

[0081] The process gas is conducted away from the PF-QT via line **151**. Typically, this stream is collected from the overhead of the quench tower, such as from the overhead of quench tower **147**. When utilizing the specified hydrocarbon feed and the specified steam cracker conditions, the process stream can include, for example, about 10 wt. % or greater of C₂₊ olefin, about 1 wt. % or greater of C₆₊ aromatic hydrocarbon, about 0.1 wt. % or greater of diolefin, saturated hydrocarbon, molecular hydrogen, acetylene, CO₂, aldehyde, and C₁₊ mercaptan.

[0082] Conventional PF-QTs can be used, but the invention is not limited thereto. Suitable primary fractionators and associated equipment are described in U.S. Pat. No.

8,083,931 and U.S. Patent Publication No. 2016/0376511, which are incorporated by reference herein.

Oil Water Separator

[0083] As shown in FIG. 2, oil-water separator **201** can be utilized to separate from pygas stream **149** a primarily liquid-phase aqueous stream and a primarily liquid-phase pygas stream. The separated pygas stream (typically with some remaining water) may be transferred via line **203** to pygas stripper **205** for further processing (stripping). Stripped pygas, typically comprising C₅ - C₁₀ hydrocarbons, is transferred via line **207** to gasoline hydrogenation unit **209** to produce various gasoline products conducted away via one or more of lines **211**. Water and light hydrocarbons can be removed from the top of pygas stripper **205** and recycled via line **213** to the PF-QT. Water that is removed in the pygas stripper may also be transferred to downstream processes or to waste water.

[0084] The primarily liquid-phase aqueous streams from the oil-water separator **201** and/or the pygas stripper may be recycled via line **215**, e.g., for use in one or more of the desalter, quench tower, or other processes. Alternatively or in addition, one or more of these primarily liquid-phase aqueous streams may be sent via line **217** to sour water stripper **219** to remove hydrogen sulfide, ammonia, and other impurities. Sour water stripping generally provides for degasification of sour water removing light hydrocarbons and remaining hydrogen. The sour water stripper may be a steam-reboiled distillation column allowing for the overhead stripping of hydrogen sulfide and ammonia through line **221**. Once the acid gas and ammonia have been removed, the clean water can be recycled (not shown) or transferred via line **223** to dilution steam generator **225** to provide steam via line **227** to the steam cracker. The dilution steam generator may also produce a primarily liquid-phase aqueous stream that can be removed via line **229**.

Light Hydrocarbon Recovery

[0085] Recovery of light hydrocarbon from the process gas can be carried out in a light hydrocarbon recovery train, such as that shown in FIG. 3. Process gas **151** (from FIG. 1) is compressed in one or more stages of process gas compressor **301**. The compressed process gas is transferred via line **303** to an acidic gas removal system that typically comprises at least one amine tower and/or at least one caustic tower. A purified process gas is conducted away via line **315**. Amine tower **305** may accept a stream **307** comprising a lean solution of one or more light amines. At least a portion of acid gases in the process gas are transferred to the lean amine solution to form a rich amine solution, which is conducted away via line **309**. After exiting the

amine tower, a partially-purified process gas may be passed through line **311** to caustic tower **313**, for additional purification, such as with an aqueous hydroxide solution, e.g. aq. sodium hydroxide, to further decrease the content of acidic gasses. A purified process gas is conducted away via line **315**.

5 Refinery and Petrochemical Process Streams

[0086] Although it is not required, the invention is compatible with combining the process gas (or one or more streams derived therefrom) with one or more refinery and/or petrochemical process streams, e.g., processes for producing one or more of fuels, lubricating oils, and petrochemicals. Doing so has been found to be efficient, especially when the available refinery streams contain molecular hydrogen and/or C₂ to C₄ olefin. For example, during an interval of diminished process gas flow, excess capacity in process gas treatment and separation stages can be utilized for (i) removing one or more desired products, e.g., C₂ – C₄ olefin, from the refinery and/or petrochemical streams and (ii) optionally recycling any remaining portion of the refinery and/or petrochemical streams (e.g., a portion comprising saturated hydrocarbon) for cracking as steam cracking furnace feed and/or combustion in steam cracking furnace burners, burners in other furnaces, etc. The process gas (or a stream derived therefrom) can be combined with one or more refinery and/or petrochemical process streams upstream and/or downstream of compressor trains **301** and/or **355**. Alternatively, or in addition, one or more of the indicated streams can be combined in between one or more stages of compressor trains **301** and/or **355**, e.g., when compressor **355** is a stage of compressor **301**.

[0087] Suitable refinery and petrochemical streams include those obtained or derived from one or more of cracking; hydroprocessing; alcohol production and/or alcohol conversion; reforming; conversion of natural gas to olefin; polymerization, including oligomerization; hydrocarbon combustion; and hydrocarbon distillation. Representative cracking processes include thermal and/or catalytic cracking, such as fluidized catalytic cracking. Representative hydroprocessing processes include catalytic and/or non-catalytic hydroprocessing, e.g., one or more of hydrotreating, hydrogenation (including hydrodearomatization), hydrodewaxing, dehydrogenation, hydrocracking, hydro-isomerization, and/or ring opening. Representative alcohol production and/or alcohol conversion processes include, e.g., catalytic and/or non-catalytic processes, such as alcohol synthesis processes (including oxo-alcohol processes) and alcohol conversion processes such as catalytic and/or non-catalytic alcohol dehydration.

[0088] In certain aspects, the process gas is combined with a light hydrocarbon gas obtained from a fluidized catalytic cracking (FCC) process, e.g., a process gas derived from an

FCC fractionator overhead. Suitable fluidized catalytic crackers and equipment associated therewith and processes for operating same can include those disclosed in Handbook of Petroleum Refining Processes, 2d Ed., R.A. Meyers, 3.3-3.111, McGraw-Hill, but the invention is not limited thereto. For example, a refinery stream comprising a light hydrocarbon product
5 derived from an FCC process, such as from an FCC fractionator overhead, can be combined (not shown) with the process gas at one or more locations in the processes illustrated by FIG. 1, such as by introducing the light hydrocarbon product into one or more of lines **151, 303, 311, 315, 319, 357, 361, 367, and 369**; at least one stage of compression trains **301** and/or **355**; and one or more of vessels **305, 313, 359, and 363**. The location in the process at which the light
10 hydrocarbon product is introduced may depend mainly on the types and amounts of impurities present therein. For example, besides light olefin, the light hydrocarbon product can contain one or more of molecular hydrogen, methane, ethane, propane, butanes, ammonia, carbon dioxide, arsine, mercury, hydrogen sulfide, carbonyl sulfide, mercaptans, and carbon disulfide, oxygenates and water.

[0089] In certain aspects, the light hydrocarbon product is treated to at least partially-remove one or more of the indicated non-olefinic compounds. The pretreatment can include, e.g., demethanizing the light hydrocarbon product in one or more demethanizers, to produce a tail gas and a demethanized C₂₊ product. Conventional demethanizers can be used, e.g., one or more cryogenic demethanizers and/or one or more absorption demethanizers, but the
20 invention is not limited thereto. Additional pretreatment stages can be used, e.g., for removing other non-hydrocarbon compounds from the light hydrocarbon product and/or the demethanized C₂₊ product. Such additional pretreatment stages can include stages for removing at least a portion of one or more of ammonia, carbon dioxide, arsine, mercury, hydrogen sulfide, carbonyl sulfide, mercaptans, and carbon disulfide, oxygenates, and water.

25 The pretreated light hydrocarbon product can be introduced as indicated into process gas and/or streams derived from the process gas.

[0090] Alternatively or in addition, at least a portion of one or more of the indicated one or more refinery and/or petrochemical process streams can be combined with feed to the steam cracking furnace, e.g., with one or more of a hydrocarbon feed, a desalted feed, a preheated
30 feed, and the pyrolysis feed. Advantageously, this can be carried out with little or no pretreatment of the refinery and/or petrochemical process streams.

[0091] Certain aspects will now be described in more detail that do not include introducing a refinery gas and/or petrochemical gas into the recovery facility. The invention

is not limited to these aspects, and this description should not be interpreted as excluding other aspects within the broader scope of the invention.

Product and Co-Product Separation and Recovery

[0092] The purified process gas may be passed to one or more fractionation towers for separation of various hydrocarbon streams before further purification. Separator **317** is utilized to separate from the upgraded process gas at least (i) a stream comprising molecular hydrogen, methane and C₂ hydrocarbons (with some C₃) removed via line **319**; and (ii) a stream comprising C₃₊ hydrocarbon, removed via line **321**. Fractionator **323** is utilized to separate from the stream comprising C₃₊ hydrocarbons at least (i) a stream comprising C₃ hydrocarbon, removed via line **325**, and (ii) a stream comprising C₄₊ hydrocarbon, removed via line **327**. Fractionator **329** is utilized to separate from the stream comprising C₄₊ hydrocarbon at least (i) a stream comprising C₄ hydrocarbon, removed via line **331**, and (ii) a stream comprising C₅₊ hydrocarbon, removed via line **333**. At least a portion of the stripped pygas of line **207** can be combined with at least a portion of the stream of line **333**. The combined stream can then be conducted to through gasoline hydrogenation unit **209** to produce various gasoline products **211** and various products **335**, e.g., that can be sent away.

[0093] The stream comprising C₃ hydrocarbon is typically conducted via line **325** to further processing stages which may include (i) contaminant-removal bed **337**, then through line **339** to (ii) arsine bed **341**, and through line **343** to (iii) methyl acetylene and propadiene (MAPD) converter **345** for hydrogenation. The purified stream comprising C₃ hydrocarbons is conducted via **347** to C₃ splitter **349** (e.g., a fractionator) for separation of at least propylene (sent away via line **351**) and propane (sent away via line **353**). Propane of line **353** may be recycled for further cracking or used in other refinery processes.

[0094] The stream conducted away from separator **317** via line **319** is transferred to compressor **355** for additional compression (e.g., compressor **355** is located downstream of compressor **301**, such as a downstream compression stage of compressor **301**). From compressor **355** a stream comprising compressed molecular hydrogen, methane and C₂ hydrocarbons (with some C₃₊) is conducted via line **357** to a series of purifications which may include (i) contaminant-removal bed **359**, then through line **361** to (ii) arsine-removal bed **363**, and then through line **365** to (iii) C₂ acetylene converter **367**. The purified stream comprising molecular hydrogen, methane, ethane, ethylene, and some C₃₊ is passed through line **369** to separator **371**. Separator **371** is utilized to separate from at least a portion of the purified stream of line **369** at least (i) a first stream comprising molecular hydrogen and methane, removed via

line **373**; and (ii) a second stream comprising C₂ hydrocarbon, this second stream being transferred via line **381** to fractionator **383**. Fractionator **383** is used to separate from this second stream (i) any residual C₃₊, e.g., for recycle via line **385** to line **325** which feeds contaminant-removal bed **337**; and (ii) a stream comprising purified C₂ hydrocarbon, which is removed via line **387** to C₂ splitter **389**. C₂ splitter **389** is utilized to separate from the purified C₂ hydrocarbon at least (i) ethylene (sent away via line **391**) and (ii) ethane (sent away via line **393**). Ethane may be recycled for further cracking or used in other refinery processes. Additional separations are optionally carried out, e.g., utilizing separator **375** to separate from the tail gas stream of line **373** at least (i) methane, removed via line **377** and (ii) molecular hydrogen, removed via line **379**. At least a portion of the separated methane may be used as fuel gas and/or steam cracked again for the production of syngas and hydrogen. At least a portion of the separated molecular hydrogen can be recycled to the clean fuels unit as a hydrogen source in one or more SCT hydroprocessing beds.

Clean Fuels Unit

[0095] Turning again to FIG. 1, a bottoms stream comprising SCT can be conducted away via line **129** from the tar knock-out drum **127** and further processed in a clean fuels unit **131**. SCT can be a highly aromatic product with a T₅₀ boiling point similar to a vacuum gas oil and/or a vacuum resid fraction. SCT can be difficult to process using a fixed bed reactor because various molecules within the SCT are highly reactive, leading to fouling and operability issues. Such processing difficulties can be further complicated, for example, by the high viscosity of the feed, the presence of coke fines, and/or other properties related to the composition of SCT.

[0096] The clean fuels unit may be a hydroprocessing unit in which SCT, a utility fluid, treat gas including hydrogen, and catalyst are combined under hydroprocessing conditions to produce clean fuels product (upgraded SCT) having improved blending characteristics with other heavy hydrocarbons such as fuel oil. The clean fuels unit may further remove particulates, sulfur and other impurities to provide a clean fuels product that is compatible with fuel oils.

[0097] Besides the bottoms stream that is conducted away via line **129**, clean fuels unit **131** also accepts lean amine stream **133**. After hydroprocessing and removal of sulfurous and other impurities clean fuels product **137** (typically a hydroprocessed SCT) is produced along with rich amine stream **135** containing removed sulfur impurities. Unexpectedly, for a wide variety of raw feeds, e.g., a wide variety of medium and/or heavy crude oils, the rich amine solution recovered from clean fuels unit **131** and the rich amines solution recovered from amine

tower **305** have compositions of sufficient similarity for these streams to be combined for regeneration together in an amine regenerator. A regenerated amine solution is recovered, divided, and recycled as lean amine solution to each of clean fuels unit **131** and amine tower **305**. Doing so is efficient and cost-effective, e.g., in obviating the need for separate amine regeneration facilities for clean fuels unit **131** and amine tower **305**.

[0098] At least a portion of any solids removed from the bottoms stream from tar knock-out drum **127** can be conducted away (not shown) before and/or during SCT processing. SCT hydroprocessing is typically carried out in clean fuels unit **131** in the presence of utility fluid (solvent), treat gas (a source of hydrogen), and hydroprocessing catalyst. Typically, the clean fuels unit includes removing at least a portion of any solids as may be present in the SCT. SCT hydroprocessing can occur in one or more hydroprocessing stages, the stages comprising one or more hydroprocessing vessels or zones downstream of the steam cracker, and typically downstream of the tar knock-out drum.

[0099] Conventional SCT hydroprocessing (process conditions, process and apparatus configurations, catalysts, etc.) can be used, but the invention is not limited thereto. Examples of suitable SCT hydroprocessing are disclosed, e.g., in P.C.T Patent Application Publications Nos. WO 2013/033590 and WO2018/111577; in U.S. Patent Applications Serial Nos. 62/659183 and 62/750636; and in U.S. Patents Nos. 9,777,227 and 9,809,756; each of which being incorporated herein by reference. SCT hydroprocessing catalysts and/or conditions can include one or more of hydrocracking (including selective hydrocracking), hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, hydrodearomatization, hydroisomerization, and hydrodewaxing catalysts and/or conditions.

[0100] The relative amounts of utility fluid and SCT during hydroprocessing are generally from about 20 wt. % to about 95 wt. % of the SCT and from about 5 wt. % to about 80 wt. % of the utility fluid, based on total weight of utility fluid plus SCT. For example, the relative amounts of utility fluid and SCT during hydroprocessing can be (i) from about 20 wt. % to about 90 wt. % of the SCT and from about 10 wt. % to about 80 wt. % of the utility fluid, or (ii) from about 40 wt. % to about 90 wt. % of the SCT and from about 10 wt. % to about 60 wt. % of the utility fluid. In an embodiment, the utility fluid:SCT weight ratio can be about 0.01 or greater, e.g., from about 0.05 to about 4, such as from about 0.1 to about 3, or from about 0.3 to about 1.1.

[0101] A utility fluid may include a solvent having significant aromatics content and generally, the utility fluid may also include a mixture of multi-ring compounds. The rings can

be aromatic or non-aromatic and can contain a variety of substituents and/or heteroatoms. For example, the utility fluid can contain about 40 wt. % or greater, about 45 wt. % or greater, about 50 wt. % or greater, about 55 wt. % or greater, or about 60 wt. % or greater, based on the total weight of the utility fluid, of aromatic and non-aromatic ring compounds. The utility fluid
5 can have an ASTM D86 10% distillation point of about 60°C or greater and a 90% distillation point of about 350°C or less. Optionally, the utility fluid (which can be a solvent or mixture of solvents) has an ASTM D86 10% distillation point of about 120°C or greater, 140°C or greater, or about 150°C or greater and/or an ASTM D86 90% distillation point of about 300°C or less.

[0102] As a result, it is believed, of the specified separations carried out in the desalting,

10 flash separation integrated with the steam cracking furnace, and tar knock-out drum, SCT is typically substantially free of impurities comprising calcium and/or sodium. The invention is compatible with SCT demetallation to remove at least a portion of any metals carried over to the SCT from the steam cracker effluent. Such metals might at least partially-deactivate (e.g., poison) the SCT hydroprocessing catalyst(s). Conventional demetallation processes and
15 demetallation catalyst (including one or more of centrifuging, non-sacrificial hydrodemetallization, and sacrificial hydro-demetallation) can be used, but the invention is not limited thereto. Conventional demetallation typically removes ≥ 70 wt. % of the SCT's iron-containing impurities, based on the total weight of iron-containing impurities in the SCT. Conventional demetallation also typically removes ≥ 90 wt. % of the SCT's nickel-containing
20 impurities, based on the total weight of nickel-containing impurities in the SCT. Conventional demetallation is even more effective for vanadium removal--removing ≥ 99 wt. % of the SCT's vanadium-containing impurities, based on the total weight of vanadium-containing impurities in the SCT. SCT after demetallation can have a nickel concentration (a third nickel concentration), e.g., of about 1 wppm or less, such as in the range of from about 0.01 wppm to
25 about 1wppm. Likewise, the SCT after demetallation can have a vanadium concentration (a third vanadium concentration), e.g., of about 1 wppm or less, such as in the range of from about 0.01 wppm to about 1wppm.

[0103] SCT hydroprocessing is carried out in the presence of hydrogen (typically provided as molecular hydrogen via a treat gas), SCT, utility fluid. Although relatively pure
30 molecular hydrogen can be utilized for the hydroprocessing, it is generally desirable to utilize a "treat gas" which contains sufficient molecular hydrogen for the hydroprocessing and optionally other species (e.g., nitrogen and light hydrocarbons such as methane) which generally do not adversely interfere with or affect either the reactions or the products. The treat

gas may contain about 50 vol% or greater of molecular hydrogen, such as about 75 vol% or greater, based on the total volume of treat gas conducted to the hydroprocessing stage.

[0104] The amount of molecular hydrogen supplied to the hydroprocessing stage can be from about 300 SCF/B (standard cubic feet per barrel) ($53 \text{ S m}^3/\text{m}^3$) to about 5000 SCF/B ($890 \text{ S m}^3/\text{m}^3$), in which B refers to barrel of feed to the hydroprocessing stage (e.g., tar stream plus utility fluid). For example, the amount of molecular hydrogen can be from 1000 SCF/B ($178 \text{ S m}^3/\text{m}^3$) to 3000 SCF/B ($534 \text{ S m}^3/\text{m}^3$). The amount of molecular hydrogen required to hydroprocess the SCT is less if the SCT contains higher amounts of C_{6+} olefin, for example, vinyl aromatics. Optionally, higher amounts of molecular hydrogen may be supplied, for example, when the SCT contains relatively higher amounts of sulfur.

[0105] One or more stages of SCT hydroprocessing catalysts can be used for the SCT hydroprocessing. The invention is also compatible with inter-stage separation from hydroprocessed or partially-hydroprocessed effluent of streams such as (i) hydroprocessed SCT, (ii) used treat gas, and (iii) one or more distillate boiling-range hydrocarbon-containing compositions, e.g., for use as the SCT hydroprocessing utility fluid and/or a quench oil for quenching the steam cracker effluent. Conventional catalysts may be used for SCT hydroprocessing, but the invention is not limited thereto.

[0106] The SCT generally contacts the hydroprocessing catalyst in the vessel or zone, in the presence of the utility fluid and molecular hydrogen. Catalytic hydroprocessing conditions can include, e.g., exposing the combined utility fluid and SCT to a temperature from about 50°C to about 500°C , such as from about 200°C to about 450°C , from about 220°C to about 430°C , from about 300°C to about 500°C , from about 350°C to about 430°C , or from about 350°C to about 420°C proximate to the molecular hydrogen and hydroprocessing catalyst. Liquid hourly space velocity (LHSV) of the combined utility fluid and SCT may be from about 0.1 h^{-1} to about 30 h^{-1} , or about 0.4 h^{-1} to about 25 h^{-1} , or about 0.5 h^{-1} to about 20 h^{-1} . In some embodiments, LHSV is about 5 h^{-1} or greater, or about 10 h^{-1} or greater, or about 15 h^{-1} or greater. Molecular hydrogen partial pressure during the hydroprocessing can be from about 0.1 MPa to about 8 MPa, or about 1 MPa to about 7 MPa, or about 2 MPa to about 6 MPa, or about 3 MPa to about 5 MPa. In some embodiments, the partial pressure of molecular hydrogen is about 7 MPa or less, about 6 MPa or less, about 5 MPa or less, about 4 MPa or less, about 3 MPa or less, about 2.5 MPa or less, or about 2 MPa or less. The hydroprocessing conditions can include, a pressure from about 1.5 mPA to about 13.5 mPA, or from about 2 mPA to about 12 mPA, or from about 2 mPA to about 10 mPA. The hydroprocessing conditions may further

include a molecular hydrogen consumption rate of about 53 standard cubic meters/cubic meter ($\text{S m}^3/\text{m}^3$) to about 445 $\text{S m}^3/\text{m}^3$ (300 SCF/B to 2500 SCF/B, where the denominator represents barrels of the tar stream, e.g., barrels of SCT).

[0107] When the clean fuels product (typically a hydroprocessed SCT) has improved properties compared to those of SCT, the clean fuels product **137** can be suitable for use as a fuel oil blending component. For example, the clean fuels product generally exhibits improved viscosity, solubility number, and insolubility number over the SCT and a lower sulfur content than SCT. Blending of the clean fuels product with other heavy hydrocarbons can be accomplished with little or no asphaltene precipitation, even without further processing of the clean fuels product prior to the blending. Typically the hydroprocessed SCT has a concentration CV_1 of vanadium-containing compounds, the SCT conducted to the clean fuels unit has a concentration CV_2 of vanadium-containing compounds, and the mass ratio of CV_1 to CV_2 is in the range of from 1:10 to 1:1000. Typically, the hydroprocessed SCT has a concentration has a concentration CN_1 of nickel-containing compounds, the SCT conducted to the clean fuels unit has a concentration has a concentration CN_2 of nickel-containing compounds, and the mass ratio of CN_1 to CN_2 is in the range of from 1:10 to 1:1000.

[0108] The clean fuels product may be separated into overhead, mid-cut, and bottoms by a separation device, e.g. one or more of distillation towers, vapor-liquid separators, splitters, fractionation towers, membranes, or absorbents. Describing the separated portions of the clean fuels product as overhead, mid-cut, and bottoms is not intended to preclude separation methods other than fractionating in a distillation tower. The overhead may include from about 0 wt. % to about 20 wt. % of the clean fuels product. The mid-cut may include from about 20 wt. % to about 70 wt. % of the clean fuels product. The bottoms may include from about 20 wt. % to about 70 wt. % of the clean fuels product.

[0109] In certain aspects, at least a portion of the overhead includes unused treat gas and may be recycled after removing undesirable impurities including H_2S and NH_3 . A vapor portion of the overhead may be directed through one or more amine towers which receive lean amine and conduct away rich amine. The upgraded vapor product may be recycled as a portion of the treat gas. Furthermore molecular hydrogen may be added to recycled portion to maintain the level of hydrogen entering the clean fuels unit as necessary for hydroprocessing the SCT.

EXAMPLE

Contaminant	Units	Concentration Range
Sodium Chloride	Wppm	0 – 350

Calcium Chloride	Wppm	0 – 40
Iron Chloride	Wppm	0 – 60
Nickel	Wppm	0 – 30
Vanadium	Wppm	0 – 25
Particulates	Wppm	0 – 1000
Asphaltenes	wt. %	Varies

[0110] The above table shows typical ranges for contaminants for a wide range of hydrocarbon feeds, such as raw feeds, e.g., a wide range of heavy and/or medium crude oils. It is found that utilizing the specified desalter, flash separator integrated with the steam cracking furnace, tar knock-out drum, and clean fuels unit, effectively and efficiently manages the removal of the indicated contaminants that are present in advantaged feeds that have utility as hydrocarbon feeds.

[0111] Utilizing the specified desalter may remove about 50% or more of calcium (weight basis, as calcium in its various forms), about 95% or more of sodium (weight basis, as sodium in its various forms), and about 75% or more of particulates (weight basis). Utilizing the specified flash separator may remove about 98% or more of remaining calcium carried over to the steam cracking feed from the desalted feed, about 98% or more of remaining sodium (weight basis, as sodium in its various forms), about 99% or more of iron (weight basis, as iron in its various forms), about 99% or more of nickel (weight basis, as nickel in its various forms), about 95% or more of vanadium (weight basis, as vanadium in its various forms), 95% or more of residual particulates (weight basis), and about 99% or more of asphaltenes (weight basis). Some residual contaminants are trapped in coke formed in a steam cracking process and are removed during decoking of the steam cracker including residual calcium, sodium, iron, nickel, vanadium and particulates. Residual vanadium may pass through the steam cracker, and be removed with accumulated SCT withdrawn from the tar knock-out drum, or from the primary fractionator when a tar knock-out drum is not used. Asphaltenes may be formed at various locations in the process, and can be removed with accumulated SCT withdrawn from the tar knock-out drum, or from the primary fractionator when a tar knock-out drum is not used. Processing in the clean fuels unit (e.g., by demetallation or other processes in the clean fuels unit) may reduce the quantity of iron in the SCT by 70% or more (weight basis, as iron in its various forms), nickel by 90% or more (weight basis, as nickel in its various forms), vanadium by 99% or more (weight basis, as vanadium in its various forms), particulates by 95% or more

(weight basis), and asphaltenes by 90% or more (weight basis), thus producing a clean fuels product with contaminant levels reduced to that which acceptable for blending into fuel oil. In one example, the clean fuels unit removed 95% of coke particulates (weight basis) in the SCT, 99+% of polymer particulates (weight basis), and 88% of asphaltene particulates.

5 **[0112]** Overall, it has been found that removal of impurities present in advantaged feeds used as hydrocarbon feeds, including hydrocarbon feeds comprising heavy hydrocarbon, can be accomplished by one or more of: (i) desalting the hydrocarbon feed, (ii) preheating the desalted feed in the convection section of the steam cracker, (iii) introducing steam into the preheated feed to produce a steam cracking feed, (iv) introducing the steam cracking feed to a
10 flash separator to separate a pyrolysis feed, (v) pyrolysing at least a portion of the pyrolysis feed to produce a steam cracker effluent, (vi) separating from the steam cracker effluent an SCT and a process gas comprising light olefin. Some impurities (mercaptans, arsine, CO₂) may be carried through this process and can be removed from the process gas in a recovery train. The combination of desalter, flash separator, and tar knock-out drum with a steam
15 cracker removes the majority of impurities that cause fouling and coking of reactor parts (e.g. asphaltenes, particulates, and impurities being and/or containing the various forms of sodium, calcium, vanadium, iron, and nickel as are found in advantaged feeds).

[0113] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range
20 not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own
25 lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0114] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. Wording preceded with the transitional phrase “comprising” includes also one or more
30 of “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” and “is”.