

PYROLYSIS TAR CONVERSION

PRIORITY CLAIM

[0001] This application claims priority to and the benefit of U.S. Patent Application
5 Serial No. 62/525,345, filed June 27, 2017; and U.S. Patent Application Serial No.
62/435,238, filed December 16, 2016, which are incorporated by reference in their entireties.

RELATED APPLICATIONS

[0002] This application is related to the following applications: U.S. Patent Application
No. _____ (Docket No. 2016EM303/2), filed December 1, 2017; U.S. Patent
10 Application Serial No. 62/561,478, filed September 21, 2017; PCT Patent Application No.
_____ (Docket No. 2017EM257 PCT), filed December 1, 2017; U.S. Patent
Application Serial No. 62/571,829, filed October 13, 2017; PCT Patent Application No.
_____ (Docket No. 2017EM321 PCT), filed December 1, 2017; PCT Patent
Application No. _____ (Docket No. 2017EM345 PCT), filed December 1, 2017; PCT
15 Patent Application No. _____ (Docket No. 2017EM346 PCT), filed December 1,
2017, which are incorporated by reference in their entireties.

FIELD

[0003] This invention relates to a process for determining the suitability of pyrolysis tar,
such as steam cracker tar, for upgrading using hydroprocessing without excessive fouling of
20 the hydroprocessing reactor. The invention also relates to sampling the pyrolysis tar,
analyzing the sample, and using the analysis to determine conditions under which the tar can
be blended, pre-treated, and/or hydroprocessed.

BACKGROUND

[0004] Pyrolysis processes, such as steam cracking, are utilized for converting saturated
25 hydrocarbons to higher-value products such as light olefins, e.g., ethylene and propylene.
Besides these useful products, hydrocarbon pyrolysis can also produce a significant amount
of relatively low-value heavy products, such as pyrolysis tar. When the pyrolysis is
conducted by steam cracking, the pyrolysis tar is identified as steam-cracker tar ("SCT").

[0005] Pyrolysis tar is a high-boiling, viscous, reactive material comprising complex
30 molecules and macromolecules that can foul equipment and conduits contacting the tar.
Pyrolysis tar typically comprises compounds which include hydrocarbon rings, e.g.,
hydrocarbons rings having hydrocarbon side chains, such as methyl and/or ethyl side chains.
Depending to some extent on features such as molecular weight, molecules and aggregates
present in the pyrolysis tar can be both relatively non-volatile and paraffin insoluble, e.g.,

pentane insoluble and heptane-insoluble. Particularly challenging pyrolysis tars contain > 1 wt. % toluene insoluble compounds. Such toluene insoluble are typically high molecular weight compounds, e.g., multi-ring structures that are also referred to as tar heavies (“TH”). These high molecular weight molecules can be generated during the pyrolysis process, and
5 their high molecular weight leads to high viscosity, which makes the tar difficult to process and transport.

[0006] Blending pyrolysis tar with lower viscosity hydrocarbons has been proposed for improved processing and transport of pyrolysis tar. However, when blending heavy hydrocarbons, fouling of processing and transport facilities can occur as a result of
10 precipitation of high molecular weight molecules, such as asphaltenes. See, e.g., U.S. Patent No. 5,871,634, which is incorporated herein by reference in its entirety. In order to mitigate asphaltene precipitation, methods to guide the blending process, e.g., methods have been developed which include determining an Insolubility Number (“I_N”) and/or Solvent Blend Number (“S_{BN}”) for the blend and/or components thereof. Successful blending can be
15 accomplished with little or substantially no asphaltene precipitation by combining the components in order of decreasing S_{BN}, so that the S_{BN} of the blend is greater than the I_N of any component of the blend. Pyrolysis tars generally have high S_{BN} > 135 and high I_N > 80 making them difficult to blend with other heavy hydrocarbons without precipitating asphaltenes. Pyrolysis tars having I_N > 100, e.g., > 110, e.g., > 130, are particularly difficult
20 to blend without phase separation occurring.

[0007] Attempts at pyrolysis tar hydroprocessing to reduce viscosity and improve both I_N and S_{BN} have been attempted, but challenges remain—primarily resulting from fouling of process equipment. For example, hydroprocessing of neat SCT results in rapid catalyst deactivation when the hydroprocessing is carried out at a temperature in the range of about
25 250°C to 380°C, a pressure in the range of about 5400 kPa to 20,500 kPa, using a conventional hydroprocessing catalyst containing one or more of Co, Ni, or Mo. This deactivation has been attributed to the presence of TH in the SCT, which leads to the formation of undesirable deposits (e.g., coke deposits) on the hydroprocessing catalyst and the reactor internals. As the amount of these deposits increases, the yield of the desired
30 upgraded pyrolysis tar (e.g., upgraded SCT) decreases and the yield of undesirable byproducts increases. The hydroprocessing reactor pressure drop also increases, often to a point where the reactor becomes inoperable before a desired reactor run length can be achieved.

[0008] One approach taken to overcome these difficulties is disclosed in International Patent Application Publication No. WO 2013/033580, which is incorporated herein by reference in its entirety. The application discloses hydroprocessing SCT in the presence of a utility fluid comprising a significant amount of single and multi-ring aromatics to form an upgraded pyrolysis tar product. The upgraded pyrolysis tar product generally has a decreased viscosity, decreased atmospheric boiling point range, and increased hydrogen content over that of the pyrolysis tar feed, resulting in improved compatibility with fuel oil and other common blend-stocks. Additionally, efficiency advances involving recycling a portion of the upgraded pyrolysis tar product as utility fluid are described in International Patent Application Publication No. WO 2013/033590 which is also incorporated herein by reference in its entirety.

[0009] Another improvement, disclosed in U.S. Patent Application Publication No. 2015/0315496, which is incorporated herein by reference in its entirety, includes separating and recycling a mid-cut utility fluid from the upgraded pyrolysis tar product. The utility fluid comprises ≥ 10.0 wt. % aromatic and non-aromatic ring compounds and each of the following: (a) ≥ 1.0 wt. % of 1.0 ring class compounds; (b) ≥ 5.0 wt. % of 1.5 ring class compounds; (c) ≥ 5.0 wt. % of 2.0 ring class compounds; and (d) ≥ 0.1 wt. % of 5.0 ring class compounds. Improved utility fluids are also disclosed in the following patent applications, each of which is incorporated by references in its entirety. U.S. Patent Application Publication No. 2015/0368570 discloses separating and recycling a utility fluid from the upgraded pyrolysis tar product. The utility fluid contains 1-ring and/or 2-ring aromatics and has a final boiling point $\leq 430^{\circ}\text{C}$. U.S. Patent Application Publication No. 2016/0122667 discloses utility fluid which contains 2-ring and/or 3-ring aromatics and has solubility blending number (S_{BN}) ≥ 120 .

[0010] Despite these advances, there remains a need for further improvements in the hydroprocessing of pyrolysis tars, especially those having high I_{N} values, which allow the production of upgraded tar product having lower viscosity at appreciable hydroprocessing reactor run lengths.

SUMMARY

[0011] It has been discovered that pyrolysis tars can be hydroprocessed for an appreciable reactor run length without undue reactor fouling, provided the tar has a reactivity that does not exceed a reference reactivity level. Pyrolysis tar reactivity (" R_{T} ") can be determined from the tar's free radical content profile, e.g., using electron resonance spin ("ESR"). Pyrolysis tar reactivity can also be determined from the tar's aliphatic olefin content, as

indicated by bromine number ("BN") or iodine number measurements. More particularly, it has been found that for a wide range of desirable pyrolysis tar hydroprocessing conditions, a reference reactivity level can be specified for the pyrolysis tar. The reference reactivity value ("R_{Ref}") can be pre-determined and corresponds to the greatest reactivity a pyrolysis tar can have without undue reactor fouling occurring during hydroprocessing. Accordingly, the reactivity R_T of a pyrolysis tar available for processing can be compared with R_{Ref}, and processing decisions can be based on the comparison. For instance, a reference reactivity value, as determined by ESR or BN, can be specified for comparison with a reactivity R_T of a particular pyrolysis tar, where R_T is also determined by ESR or BN. When R_T is $\leq$ R_{Ref}, and particularly when R_T is $\leq$ 18 Bromine Number units, e.g., $\leq$ 12 Bromine Number units, the pyrolysis tar can be hydroprocessed with decreased reactor fouling and increased run-lengths. Advantageously, R_T can be determined using a suitably prepared pyrolysis tar sample at ambient (e.g., 25°C) temperature, even though the sample is obtained from a pyrolysis tar source, such as a tar drum, having a much greater temperature, e.g., in a range of about 140°C to 350°C. This greatly simplifies the measurement of R_T.

[0012] Accordingly, certain aspects of the invention relate to a process for upgrading a reactive hydrocarbon feed. The feed can be a hydrocarbon-containing mixture such as pyrolysis tar, e.g., SCT. At least 70 wt. % of the hydrocarbon-containing mixture has a normal boiling point of at least 290°C. In accordance with the process, a sample is isolated from the hydrocarbon mixture. The sample's reactivity R_T is determined, and R_T is compared to a predetermined reference reactivity R_{Ref}. When R_T exceeds R_{Ref}, the hydrocarbon-containing mixture, one or more of the following procedures is carried out:

(i) At least a portion of the hydrocarbon-containing mixture is thermally treated (e.g., heat-soaked) one or more times until R_T is $\leq$ R_{Ref}, after which at least a portion of the thermally treated hydrocarbon-containing mixture is conducted as pyrolysis tar feed to a hydroprocessing stage for hydroprocessing. The thermal treatment includes maintaining the hydrocarbon-containing mixture at a temperature in the range of from 150°C to 350°C for a time t_{HS} of at least 1 minute.

(ii) At least a portion of the hydrocarbon-containing mixture is blended with a sufficient amount of at least a second hydrocarbon-containing mixture to achieve an R_T that does not exceed R_{Ref}, after which at least a portion of the blend is conducted as pyrolysis tar feed to a hydroprocessing stage for hydroprocessing. At least 70 wt. % of the second hydrocarbon-containing mixture has a normal boiling point of at least 290°C.

(iii) At least a portion of the hydrocarbon-containing mixture is conducted as

pyrolysis tar feed to a hydroprocessing stage for hydroprocessing under Mild Hydroprocessing Conditions.

(iv) At least a portion of the hydrocarbon-containing mixture is conducted away.

When R_T does not exceed R_{Ref} , the hydrocarbon-containing mixture can be conducted
5 directly to the hydroprocessing without the thermal treatment, without blending, and without the need for Mild Hydroprocessing Conditions during the hydroprocessing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings are for illustrative purposes only and are not intended to limit the scope of the present invention.

10 [0014] Fig. 1 is a schematic representing a hydroprocessing reaction sequence.

[0015] Fig. 2 is a graph of the bromine number versus thermal treatment residence time at various temperatures.

[0016] Fig. 3 is a graph of a hydroprocessing reactor pressure drop versus days on stream at standard hydroprocessing conditions for tars with no thermal treatment, and two different
15 thermal treatment (heat soak) conditions.

[0017] Fig. 4 is a graph of tar aliphatic olefin content (unsaturated component) versus thermal treatment conditions.

DETAILED DESCRIPTION

[0018] A pyrolysis tar is evaluated for its reactivity to evaluate its potential for fouling
20 the reactor at desired hydroprocessing conditions. The tar's reactivity is compared to a predetermined reference activity. Pyrolysis tars having a reactivity that does not exceed the reference activity can be conducted as pyrolysis tar feed to a hydroprocessing stage operating under Standard Hydroprocessing Conditions or Mild Hydroprocessing Conditions to produce a hydroprocessed pyrolysis tar. Pyrolysis tars having a reactivity that exceeds the reference
25 activity are (i) subjected to additional processing before the hydroprocessing and/or subjected to Mild Hydroprocessing Conditions during the hydroprocessing or (ii) conducted away.

[0019] A pyrolysis tar's free radical content is an indication of its reactivity. Free radical content can be evaluated, e.g., by sampling the pyrolysis tar, such as at a temperature $T_1 \leq 350^\circ\text{C}$. The sample's temperature is raised to a predetermined temperature T_2 that is at least
30 10°C greater than T_1 , and the sample's temperature is maintained at a temperature within about $\pm 5^\circ\text{C}$ of T_2 for predetermined period of time t_h . Typically, T_2 is substantially the same as the desired hydroprocessing temperature, and t_h is substantially the same as the time during which the tar is exposed to hydroprocessing conditions during the hydroprocessing. Following this, the sample is cooled to a temperature $T_3 \leq T_1$, and the reactivity R_T of the

cooled sample is measured, e.g., using ESR, BN, etc. The tar's reactivity R_T is compared to the pre-determined reference value R_{Ref} . Typically R_T and R_{Ref} are determined using substantially the same methods and process conditions, e.g., using BN at substantially the same T_1 , T_2 , T_3 , and t_h , but this is not required. Those skilled in the art will appreciate that a correlation between measurement output and tar reactivity can be established for each of the free radical measurement methods (e.g., ESR and BN) at various measurement conditions, which if carried out would permit a comparison of R_T as determined by one measurement method (e.g., ESR) with R_{Ref} determined by another method (e.g., BN).

[0020] The comparison of R_T and R_{Ref} is used to select from among various processing options for the pyrolysis tar. For example, the comparison can be used to determine whether (a) the sampled pyrolysis tar is a suitable candidate for hydroprocessing under the specified Standard Hydroprocessing Conditions, e.g., when R_T is $\leq R_{Ref}$, such as R_T is $\leq 0.5 \cdot R_{Ref}$, or R_T is $\leq 0.1 \cdot R_{Ref}$. When R_T is $> R_{Ref}$, the available processing options include one or more of (a) subjecting the tar to the specified Mild Hydroprocessing Conditions, (b) further processing of the tar to achieve an R_T is $\leq R_{Ref}$, and then hydroprocessing the further-processed tar, and/or (c) conducting the tar away without hydroprocessing. For example, the pyrolysis tar can be conducted away when (i) the value of a hydroprocessed tar produced using Mild Hydroprocessing Conditions is not sufficient to justify the cost of the hydroprocessing and/or (ii) the value of a hydroprocessed tar is not sufficient to justify the cost of the further treatment.

[0021] Further processing of the pyrolysis tar can be carried out if desired, and can include one of more of (i) at least one blending operation and (ii) at least one thermal treatment. For example, should R_T exceed R_{Ref} , the pyrolysis tar may be blended with a second pyrolysis tar to decrease the reactivity of the blended tar into a range that does not exceed R_{Ref} . The blend can then be conducted as pyrolysis tar feed to a hydroprocessing reactor for hydroprocessing. A plurality of pyrolysis tars, including a plurality of SCTs, may be blended to produce a blended pyrolysis tar with a specific free radical profile, e.g., one exhibiting a blended sample $R_T \leq R_{Ref}$. The blending can be carried out before and/or during the hydroprocessing. For example, a blend of pyrolysis tars having an $R_T \leq R_{Ref}$ can be conducted to hydroprocessing as pyrolysis tar feed. Typically, the hydroprocessing of the pyrolysis tar feed is carried out in the presence of at least one utility fluid. When the hydroprocessing is carried out in more than one hydroprocessing stage, the hydroprocessing of at least one of the stages is carried out in the presence of the utility fluid. The pyrolysis tar feed can be combined with utility fluid at any convenient time, e.g., before and/or during

hydroprocessing. When the pyrolysis tar feed includes a blend of one or more pyrolysis tars, the pyrolysis tar feed may be combined with utility fluid at any time, e.g., one or more of before, during, and after blending.

[0022] Instead of or in addition to blending, the hydroprocessing can be carried out under the specified Mild Hydroprocessing Conditions, which when used decreases the severity of the reaction and/or slows the reaction as compared to hydroprocessing under the specified Standard Hydroprocessing Conditions. When a pyrolysis tar's R_T exceeds R_{Ref} , hydroprocessing the tar under the specified Mild Hydroprocessing Conditions lessens the potential for fouling during the hydroprocessing, but typically produces a hydroprocessed tar having properties that are not as favorable as those of hydroprocessed tars produced using the specified Standard Hydroprocessing Conditions.

[0023] Certain methods for evaluating pyrolysis tar reactivity, pyrolysis tar blending, thermal treatments of pyrolysis tar, pyrolysis tar hydroprocessing under Standard Hydroprocessing Conditions and Mild Hydroprocessing Conditions will now be described in more detail. The invention is not limited to these methods, and this descriptions is not meant to foreclose the use of other methods, apparatus, systems, etc., within the broader scope of the invention. Reference will be made to the following defined terms in this description and appended claims.

[0024] The term "pyrolysis tar" means (a) a mixture of hydrocarbons having one or more aromatic components and optionally (b) non-aromatic and/or non-hydrocarbon molecules, the mixture being derived from hydrocarbon pyrolysis, with at least 70% of the mixture having a boiling point at atmospheric pressure that is $\geq$ about 550°F (290°C). Certain pyrolysis tars have an initial boiling point $\geq$ 200°C. For certain pyrolysis tars, $\geq$ 90.0 wt. % of the pyrolysis tar has a boiling point at atmospheric pressure $\geq$ 550°F (290°C). Pyrolysis tar can comprise, e.g., $\geq$ 50.0 wt. %, e.g., $\geq$ 75.0 wt. %, such as $\geq$ 90.0 wt. %, based on the weight of the pyrolysis tar, of hydrocarbon molecules (including mixtures and aggregates thereof) having (i) one or more aromatic components, and (ii) a number of carbon atoms $\geq$ about 15. Pyrolysis tar generally has a metals content, $\leq 1.0 \times 10^3$ ppmw, based on the weight of the pyrolysis tar, which is an amount of metals that is far less than that found in crude oil (or crude oil components) of the same average viscosity. "SCT" means pyrolysis tar obtained from steam cracking.

[0025] "Aliphatic olefin component" or "aliphatic olefin content" means the portion of the tar that contains hydrocarbon molecules having olefin unsaturation (at least one unsaturated carbon that is not an aromatic unsaturation) where the hydrocarbon may or may

not also have aromatic unsaturation. For instance, a vinyl hydrocarbon like styrene, if present in the pyrolysis tar, would be included aliphatic olefin content.

[0026] “Tar Heavies” (TH) are a product of hydrocarbon pyrolysis having an atmospheric boiling point $\geq 565^{\circ}\text{C}$ and comprising ≥ 5.0 wt. % of molecules having a plurality of aromatic cores based on the weight of the product. The TH are typically solid at 25°C and generally include the fraction of SCT that is not soluble in a 5:1 (vol.:vol.) ratio of n-pentane: SCT at 25°C . TH generally includes asphaltenes and other high molecular weight molecules.

[0027] Aspects of the invention will now be described which include (i) establishing an R_{Ref} for desired hydroprocessing conditions, (ii) obtaining a sample of a pyrolysis tar, (iii) measuring R_{T} of a suitably-prepared sample of the pyrolysis tar, and (iv) comparing R_{T} to R_{Ref} . For tars having an $R_{\text{T}} > R_{\text{Ref}}$, certain aspects will be described which include exposing at least a portion of the tar to one or more thermal treatments (e.g., heat soaks) to decrease the tar's R_{T} into a range that does not exceed R_{Ref} . As an alternative or in addition to these aspects, other aspects will be described which include blending at least a portion of a pyrolysis tar having an $R_{\text{T}} > R_{\text{Ref}}$ with at least a second pyrolysis tar to achieve a desired radical profile for the blend, as indicated, e.g., by the blend having an R_{T} that does not exceed R_{Ref} . As an alternative or in addition to any of the foregoing aspects, other aspects will be described which include hydroprocessing at least a portion of a pyrolysis tar (or a blend of pyrolysis tars) having an $R_{\text{T}} > R_{\text{Ref}}$ using Mild Hydroprocessing Conditions. Alternatively or in addition to any of the foregoing aspects, at least a portion of a tar or tar blend having an $R_{\text{T}} > R_{\text{Ref}}$ can be conducted away without hydroprocessing. Representative pyrolysis tars that may benefit from the foregoing processing will now be described in more detail. The invention is not limited to these pyrolysis tars, and this description is not meant to foreclose other pyrolysis tars within the broader scope of the invention.

Pyrolysis Tar

[0028] Pyrolysis tar is a product or by-product of hydrocarbon pyrolysis, e.g., steam cracking. Effluent from the pyrolysis is typically in the form of a mixture comprising unreacted feed, unsaturated hydrocarbon produced from the feed during the pyrolysis, and pyrolysis tar. The pyrolysis tar typically comprises ≥ 90 wt. %, of the pyrolysis effluent's molecules having an atmospheric boiling point of $\geq 290^{\circ}\text{C}$. Besides hydrocarbon, the feed to pyrolysis optionally further comprise diluent, e.g., one or more of nitrogen, water, etc. Steam cracking, which produces SCT, is a form of pyrolysis which uses a diluent comprising an appreciable amount of steam. Steam cracking will now be described in more detail. The invention is not limited to pyrolysis tars produced by steam cracking, and this description is

not meant to foreclose producing pyrolysis tar by other pyrolysis methods within the broader scope of the invention.

Steam Cracking

[0029] A steam cracking plant typically comprises a furnace facility for producing steam
5 cracking effluent and a recovery facility for removing from the steam cracking effluent a plurality of products and by-products, e.g., light olefin and pyrolysis tar. The furnace facility generally includes a plurality of steam cracking furnaces. Steam cracking furnaces typically include two main sections: a convection section and a radiant section, the radiant section typically containing fired heaters. Flue gas from the fired heaters is conveyed out of the
10 radiant section to the convection section. The flue gas flows through the convection section and is then conducted away, e.g., to one or more treatments for removing combustion by-products such as NO_x. Hydrocarbon is introduced into tubular coils (convection coils) located in the convection section. Steam is also introduced into the coils, where it combines with the hydrocarbon to produce a steam cracking feed. The combination of indirect heating
15 by the flue gas and direct heating by the steam leads to vaporization of at least a portion of the steam cracking feed's hydrocarbon component. The steam cracking feed containing the vaporized hydrocarbon component is then transferred from the convection coils to tubular radiant tubes located in the radiant section. Indirect heating of the steam cracking feed in the radiant tubes results in cracking of at least a portion of the steam cracking feed's hydrocarbon
20 component. Steam cracking conditions in the radiant section, can include, e.g., one or more of (i) a temperature in the range of 760°C to 880°C, (ii) a pressure in the range of from 1.0 to 5.0 bars (absolute), or (iii) a cracking residence time in the range of from 0.10 to 2.0 seconds.

[0030] Steam cracking effluent is conducted out of the radiant section and is quenched, typically with water or quench oil. The quenched steam cracking effluent ("quenched
25 effluent") is conducted away from the furnace facility to the recovery facility, for separation and recovery of reacted and unreacted components of the steam cracking feed. The recovery facility typically includes at least one separation stage, e.g., for separating from the quenched effluent one or more of light olefin, steam cracker naphtha, steam cracker gas oil, SCT, water, light saturated hydrocarbon, molecular hydrogen, etc.

30 [0031] Steam cracking feed typically comprises hydrocarbon and steam, e.g., ≥ 10.0 wt. % hydrocarbon, based on the weight of the steam cracking feed, e.g., ≥ 25.0 wt. %, ≥ 50.0 wt. %, such as ≥ 65 wt. %. Although the hydrocarbon can comprise one or more light hydrocarbons such as methane, ethane, propane, butane etc., it can be particularly advantageous to include a significant amount of higher molecular weight hydrocarbon.

While doing so typically decreases feed cost, steam cracking such a feed typically increases the amount of SCT in the steam cracking effluent. One suitable steam cracking feed comprises ≥ 1.0 wt. %, e.g., ≥ 10 wt. %, such as ≥ 25.0 wt. %, or ≥ 50.0 wt. % (based on the weight of the steam cracking feed) of hydrocarbon compounds that are in the liquid and/or solid phase at ambient temperature and atmospheric pressure.

[0032] The steam cracking feed comprises water and hydrocarbon. The hydrocarbon typically comprises ≥ 10.0 wt. %, e.g., ≥ 50.0 wt. %, such as ≥ 90.0 wt. % (based on the weight of the hydrocarbon) of one or more of naphtha, gas oil, vacuum gas oil, waxy residues, atmospheric residues, residue admixtures, or crude oil; including those comprising $\geq$ about 0.1 wt. % asphaltenes. When the hydrocarbon includes crude oil and/or one or more fractions thereof, the crude oil is optionally desalted prior to being included in the steam cracking feed. A crude oil fraction can be produced by separating atmospheric pipestill (“APS”) bottoms from a crude oil followed by vacuum pipestill (“VPS”) treatment of the APS bottoms.

[0033] Suitable crude oils include, e.g., high-sulfur virgin crude oils, such as those rich in polycyclic aromatics. For example, the steam cracking feed’s hydrocarbon can include ≥ 90.0 wt. % of one or more crude oils and/or one or more crude oil fractions, such as those obtained from an atmospheric APS and/or VPS; waxy residues; atmospheric residues; naphthas contaminated with crude; various residue admixtures; and SCT.

[0034] SCT is typically removed from the quenched effluent in one or more separation stages, e.g., as a bottoms stream from one or more tar drums. Such a bottoms stream typically comprises ≥ 90.0 wt. % SCT, based on the weight of the bottoms stream. The SCT can have, e.g., a boiling range $\geq$ about 550°F (290°C) and can comprise molecules and mixtures thereof having a number of carbon atoms $\geq$ about 15. Typically, quenched effluent includes ≥ 1.0 wt. % of C₂ unsaturates and ≥ 0.1 wt. % of TH, the weight percents being based on the weight of the pyrolysis effluent. It is also typical for the quenched effluent to comprise ≥ 0.5 wt. % of TH, such as ≥ 1.0 wt. % TH.

[0035] Representative SCTs will now be described in more detail. The invention is not limited to these SCTs, and this description is not meant to foreclose the processing of other pyrolysis tars within the broader scope of the invention.

Steam Cracker Tar

[0036] Conventional separation equipment can be used for separating SCT and other products and by-products from the quenched steam cracking effluent, e.g., one or more flash drums, knock out drums, fractionators, water-quench towers, indirect condensers, etc.

Suitable separation stages are described in U.S. Patent No. 8,083,931, for example. SCT can be obtained from the quenched effluent itself and/or from one or more streams that have been separated from the quenched effluent. For example, SCT can be obtained from a steam cracker gas oil stream and/or a bottoms stream of the steam cracker's primary fractionator, from flash-drum bottoms (e.g., the bottoms of one or more flash drums located downstream of the pyrolysis furnace and upstream of the primary fractionator), or a combination thereof. Certain SCTs are a mixture of primary fractionator bottoms and tar knock-out drum bottoms.

[0037] A typical SCT stream from one or more of these sources generally contains ≥ 90.0 wt. % of SCT, based on the weight of the stream, e.g., ≥ 95.0 wt. %, such as ≥ 99.0 wt. %. More than 90 wt. % of the remainder of the SCT stream's weight (e.g., the part of the stream that is not SCT, if any) is typically particulates. The SCT typically includes ≥ 50.0 wt. %, e.g., ≥ 75.0 wt. %, such as ≥ 90.0 wt. % of the quenched effluent's TH, based on the total weight TH in the quenched effluent.

[0038] The TH are typically in the form of aggregates which include hydrogen and carbon and which have an average size in the range of 10.0 nm to 300.0 nm in at least one dimension and an average number of carbon atoms ≥ 50 . Generally, the TH comprise ≥ 50.0 wt. %, e.g., ≥ 80.0 wt. %, such as ≥ 90.0 wt. % of aggregates having a C:H atomic ratio in the range of from 1.0 to 1.8, a molecular weight in the range of 250 to 5000, and a melting point in the range of 100°C to 700°C.

[0039] Representative SCTs typically have (i) a TH content in the range of from 5.0 wt. % to 40.0 wt. %, based on the weight of the SCT, (ii) an API gravity (measured at a temperature of 15.8°C) of $\leq 8.5^\circ\text{API}$, such as $\leq 8.0^\circ\text{API}$, or $\leq 7.5^\circ\text{API}$; and (iii) a 50°C viscosity in the range of 200 cSt to 1.0×10^7 cSt, as determined by A.S.T.M. D445. The SCT can have, e.g., a sulfur content that is > 0.5 wt. %, e.g., in the range of 0.5 wt. % to 7.0 wt. %, based on the weight of the SCT. In aspects where steam cracking feed does not contain an appreciable amount of sulfur, the SCT can comprise ≤ 0.5 wt. % sulfur, e.g., ≤ 0.1 wt. %, such as ≤ 0.05 wt. % sulfur, based on the weight of the SCT.

[0040] The SCT can have, e.g., (i) a sulfur content in the range of 0.5 wt. % to 7.0 wt. %, based on the weight of the SCT; (ii) a TH content in the range of from 5.0 wt. % to 40.0 wt. %, based on the weight of the SCT; (iii) a density at 15°C in the range of 1.01 g/cm³ to 1.19 g/cm³, e.g., in the range of 1.07 g/cm³ to 1.18 g/cm³; and (iv) a 50°C viscosity in the range of 200 cSt to 1.0×10^7 cSt. The specified hydroprocessing is particularly advantageous for SCTs having density at 15°C that is ≥ 1.10 g/cm³, e.g., ≥ 1.12 g/cm³, ≥ 1.14 g/cm³, ≥ 1.16 g/cm³, or ≥ 1.17 g/cm³. Optionally, the SCT has a kinematic viscosity at 50°C $\geq 1.0 \times 10^4$

cSt, such as $\geq 1.0 \times 10^5$ cSt, or $\geq 1.0 \times 10^6$ cSt, or even $\geq 1.0 \times 10^7$ cSt. Optionally, the SCT has an $I_N > 80$ and > 70 wt. % of the pyrolysis tar's molecules have an atmospheric boiling point of $\geq 290^\circ\text{C}$.

[0041] Optionally, the SCT has a normal boiling point $\geq 290^\circ\text{C}$, a viscosity at $15^\circ\text{C} \geq 1 \times 10^4$ cSt, and a density $\geq 1.1 \text{ g/cm}^3$. The SCT can be a mixture which includes a first SCT and one or more additional pyrolysis tars, e.g., a combination of the first SCT and one or more additional SCTs. When the SCT is a mixture, it is typical for at least 70 wt. % of the mixture to have a normal boiling point of at least 290°C , and include free radicals which contribute to the tar's reactivity under hydroprocessing conditions. When the mixture comprises a first and second pyrolysis tars (one or more of which is optionally an SCT) ≥ 90 wt. % of the second pyrolysis tar optionally has a normal boiling point $\geq 290^\circ\text{C}$.

[0042] It has been found that an increase in reactor fouling occurs during hydroprocessing when the SCT contains an excessive amount of free radicals. In order to lessen the amount of reactor fouling as might occur during SCT hydroprocessing in the presence of the specified utility fluid under the specified hydroprocessing conditions, it is beneficial for an SCT feed to the hydroprocessor to have an olefin content of ≤ 10.0 wt. % (based on the weight of the SCT), e.g., ≤ 5.0 wt. %, such as ≤ 2.0 wt. %. More particularly, it has been observed that less reactor fouling occurs during the hydroprocessing when the SCT has (i) an amount of vinyl aromatics of ≤ 5.0 wt. % (based on the weight of the SCT), e.g., ≤ 3 wt. %, such as ≤ 2.0 wt. % and/or (ii) an amount of aggregates which incorporate vinyl aromatics of ≤ 5.0 wt. % (based on the weight of the SCT), e.g., ≤ 3 wt. %, such as ≤ 2.0 wt. %. Certain aspects of the invention are based in part on the development of a process which includes steps for (i) determining the reactivity R_T of an SCT, (ii) comparing the SCT's R_T to a pre-determined reference reactivity R_{Ref} , and then using the comparison to select processing options for the SCT which lessen the free radical content. These aspects will now be described in more detail. The invention is not limited to these aspects, and this description is not meant to foreclose other aspects within the broader scope of the invention.

Determining Pyrolysis Tar Reactivity

[0043] The fouling tendency (e.g., the reactivity) of a pyrolysis tar during hydroprocessing varies from one batch to another depending upon, for example, the pyrolysis tar's thermal history during pyrolysis and thereafter. Pyrolysis tar reactivity has been found to be well-correlated with the tar's free radical content, particularly the tar's aliphatic olefin content, and more particularly the tar's vinyl aromatic content. Reactivity R_T and reference reactivity R_{Ref} can be determined by any convenient method, including conventional methods

such as ESR and BN. Typically, the method selected for measuring R_T is substantially the same as that utilized for establishing R_{Ref} , but this is not required.

Determining R_T by ESR

[0044] The tendency of a pyrolysis tar to foul a hydroprocessing reactor under
 5 hydroprocessing conditions has been found to be correlated with the tar's free radical content as measured at ambient temperature by ESR. Accordingly, in certain aspects a pyrolysis tar, e.g., an SCT, is provided at a temperature in a range of about 140°C to 350°C. A sample is withdrawn from the tar. Those skilled in the art will appreciate that the amount of tar in the sample is not critical provided the sample contains sufficient tar for carrying out the ESR
 10 measurement. The sample is heated to a temperature that exceeds T_1 by at least 10°C for a heating time t_h , after which time the sample is cooled to a temperature T_3 that is $\leq T_1$. An ESR measurement is used to determine the free radical content of the cooled sample. The ESR measurement can be carried out at a temperature $\leq T_1$, e.g., at ambient temperature, typically about 25°C. The ESR measurement of the cooled sample can be carried out as
 15 follows.

[0045] A suitable amount, e.g., 5.5 ± 1 mg, of the cooled pyrolysis tar is loaded into a glass capillary having a diameter of about 1.1 mm. The sample occupies about 10 mm of the capillary's length. Although the capillary can be loaded at any convenient temperature $T_1 \leq 350^\circ\text{C}$, it can be beneficial to expose the pyrolysis tar to a temperature of 100°C for 1 hr. in
 20 an oven in order to increase the viscosity of the tar for easier capillary loading. The loaded capillary is weighed and then placed inside a glass tube of 2 mm diameter $\times$ 30 mm length. The glass tube is purged with nitrogen for at least about 15 seconds and then sealed by exposing each end of the tube to a burner. Purging is believed to effectively limit the influence of oxygen on the free radical measurement.

[0046] While not wishing to be bound by any theory or model, it is believed that heating the pyrolysis tar sample to a temperature $T_2 \geq T_1 + 10^\circ\text{C}$, for the specified heating time t_h produces additional free radicals in the sample, which are then "frozen-in" when the sample is cooled. Heating rate is adjusted so that the sample increases in temperature to substantially achieve thermal equilibrium at temperature T_2 at the end of a first ramp time that is $\leq t_h$, e.g.,
 25 $\leq 0.75 \cdot t_h$, such as $\leq 0.5 \cdot t_h$, or $\leq 0.25 \cdot t_h$, or $\leq 0.1 \cdot t_h$. Temperature T_2 is typically $\geq 375^\circ\text{C}$, e.g., $\geq 400^\circ\text{C}$, or $\geq 420^\circ\text{C}$, or $\geq 440^\circ\text{C}$, or $\geq 460^\circ\text{C}$, or $\geq 480^\circ\text{C}$, or $\geq 500^\circ\text{C}$. Heating time t_h is typically ≥ 30 seconds, e.g., ≥ 1.0 minute, such as ≥ 1.5 minutes, or ≥ 2.0 minutes, or ≥ 2.5 minutes, or ≥ 3.0 minutes, or ≥ 5.0 minutes, or ≥ 7.5 minutes, or ≥ 10.0 minutes, or ≥ 15.0 minutes, or ≥ 20.0 minutes, or ≥ 30.0 minutes, or ≥ 40.0 minutes. In certain aspects,
 30

temperature T_2 is substantially the same as the average bed temperature of the hydroprocessing reactor, and t_h is substantially the same as the average residence time of the pyrolysis tar in the hydroprocessing reactor. Doing so has been found to increase the effectiveness of the comparison of R_T and R_{Ref} , particularly when R_{Ref} is established under substantially the same hydroprocessing conditions as R . Since R_T and R_{Ref} are well-correlated with pyrolysis tar free radical content as measured by ESR, they can be expressed in units of “spins per gram of pyrolysis tar”.

[0047] Sample preparation also includes cooling (e.g., quenching) the heated sample from T_2 to a temperature T_3 , wherein $T_3 \leq T_1$. Heating rate is adjusted so that the sample decreases in temperature to substantially achieve thermal equilibrium at temperature T_3 at the end of a second ramp time that is $\leq t_h$, e.g., $\leq 0.75 * t_h$, such as $\leq 0.5 * t_h$, or $\leq 0.25 * t_h$, or $\leq 0.1 * t_h$.

[0048] Suitable instruments for measuring ESR include Electron Spin Resonance Spectrometer, Model JES FA 200 (available from JEOL, Japan). The ESR measurement can be carried out at any convenient temperature $\leq T_3$, e.g., ambient temperature. The ESR spectrometer can be calibrated using, e.g., 2,2-diphenyl-1-picrylhydrazyl (DPPH).

Determining R_T by BN

[0049] Pyrolysis tar reactivity (and fouling tendency) also have been found to be well-correlated with the tar's aliphatic olefin content, especially the content of styrenic hydrocarbons and dienes. While not wishing to be bound by any particular theory, it is believed that aliphatic olefin compounds in the tar (i.e., the tar's aliphatic olefin components) have a tendency to polymerize during hydroprocessing, forming coke precursors that are capable of plugging or otherwise fouling the reactor. Fouling is more prevalent in the absence of hydrogenation by catalysts, such as in the preheater and dead volume zones of a hydroprocessing reactor. As a result, certain measures of the tar's aliphatic olefin content, e.g., BN, are well-correlated with tar reactivity, and R_T and R_{Ref} can be expressed in BN units, i.e., the amount of bromine (as Br_2) in grams consumed (e.g., by reaction and/or sorption) by 100 grams of a pyrolysis tar sample. BN can be used as a measure of pyrolysis tar free radical content in addition to or as an alternative to spins per gram as measured by ESR.

[0050] Bromine Index (“BI”) can be used instead of or in addition to BN measurements, where BI is the amount of Br_2 mass in mg consumed by 100 grams of pyrolysis tar. Conventional methods for measuring BN of a heavy hydrocarbon can be used, but the invention is not limited thereto. For example, BN of a pyrolysis tar can be determined by

extrapolation from conventional BN methods as applied to light hydrocarbon streams, such as electrochemical titration, e.g., as specified in A.S.T.M. D-1159; colorimetric titration, as specified in A.S.T.M. D-1158; and coulometric Karl Fischer titration. Preferably, the titration is carried out on a tar sample having a temperature $\leq$ ambient temperature, e.g., $\leq 25^{\circ}\text{C}$.

5 Although the cited A.S.T.M. standards are indicated for samples of lesser boiling point, it has been found that they are also applicable to measuring pyrolysis tar BN. Suitable methods for doing so are disclosed by D.J. Ruzicka and K. Vadum in Modified Method Measures Bromine Number of Heavy Fuel Oils, Oil and Gas Journal, Aug. 3, 1987, 48-50; which is incorporated by reference herein in its entirety.

10 **[0051]** Accordingly, in certain aspects a pyrolysis tar, e.g., an SCT, is provided at a temperature in a range of about 140°C to 350°C . A sample is withdrawn from the tar. Those skilled in the art will appreciate that the amount of tar in the sample is not critical provided the sample contains sufficient tar for carrying out the BN measurement. The sample is exposed to a predetermined temperature T_2 for a predetermined time t_h , where T_2 is $\geq T_1 +$
 15 10°C . The heated sample is then cooled by exposing the sample to a temperature T_3 that is $\leq T_1$. The cooled sample's reactivity R_T is measured and the BN value is recorded. This BN value can be directly compared to an R_{Ref} expressed as a BN value. As with ESR, BN is measured on a tar basis, i.e., measured on the tar sample with little or no utility fluid, e.g., less than 15 wt. % utility fluid.

20 **[0052]** Samples of the tar can be obtained after the tar is separated from the quenched effluent, for instance sampling the tar as the liquid portion of a flash drum separator, such as sampling from line 63 from separator 61 in Fig. 1. The sample is cooled to ambient temperatures or lower, and conventional measurements taken to determine aliphatic olefin contents, such as bromine number measurements, or iodine number measurements (A.S.T.M. D4607 method of WIJS Method or the Hübl method). If desired, Iodine Number can be
 25 used as an alternative to BN for establishing tar reactivity R_T and reference activity R_{Ref} . BN may be approximated from Iodine Number by the formula:

$$\text{BN} \sim \text{Iodine Number} * (\text{Atomic Weight of } \text{I}_2) / (\text{Atomic Weight of } \text{Br}_2).$$

[0053] R_{Ref} can be established by catalytically hydroprocessing a sequence of pyrolysis tar feeds in the presence of utility fluid and molecular hydrogen under Standard
 30 Hydroprocessing Conditions. Suitable methods for determining R_{Ref} will now be described in more detail. The invention is not limited to these methods, and this description is not meant to foreclose the use of other methods for measuring R_{Ref} within the broader scope of the invention.

Determining R_{Ref}

[0054] A reference reactivity R_{Ref} can be established for a wide range of process conditions within the Standard Hydroprocessing Conditions. Although R_{Ref} for particular process conditions (or a set of particular process conditions spanning the entire range of Standard Hydroprocessing Conditions) can be determined from modeling studies, e.g., by modeling the yield of heavy hydrocarbon deposits under selected hydroprocessing conditions, it is typically more convenient to determine R_{Ref} experimentally.

[0055] One method to determine R_{Ref} experimentally is by providing a set of approximately ten pyrolysis tars (or tar mixtures). Each pyrolysis tar in the set has an R_T different from that of the others (ideally the R_T values are substantially equally spaced), and each has an R_T , if measured by ESR, within the range of 1×10^{17} spins per gram of tar to 1×10^{20} spins per gram of tar, if measuring BN, between 15 BN to 28 BN (i.e., grams of $Br_2/100$ g sample). A table of reactivity ("R") values can be produced by hydroprocessing each pyrolysis tar in the set by hydroprocessing each tar at a plurality of selected hydroprocessing conditions within the Standard Hydroprocessing Conditions (e.g., conditions of increasing severity), and observing whether reactor fouling occurs before a pre-determined hydroprocessing time duration has elapsed. When it is desired to designate for hydroprocessing a pyrolysis tar feed that is not a member of the foregoing set under particular hydroprocessing conditions within the Standard Hydroprocessing Conditions, R_T of the pyrolysis tar feed is measured, and this value of R_T is compared to that R selected among the tabulated R_{Ref} values which most closely corresponds to the selected hydroprocessing conditions. Hydroprocessing of the designated pyrolysis tar can be carried out efficiently with little or no reactor fouling at the selected Standard Hydroprocessing Conditions when R_T is less than R_{Ref} , e.g., $\leq 75\%$ of R_{Ref} , such as $\leq 50\%$ of R_{Ref} , or $\leq 25\%$ of R_{Ref} , or $\leq 10\%$ of R_{Ref} .

[0056] As an example, when hydroprocessing representative pyrolysis tar under selected hydroprocessing conditions within the specified Standard Hydroprocessing Conditions, e.g. selected conditions which include an average bed temperature $\geq 480^\circ\text{C}$ (e.g., $\geq 500^\circ\text{C}$), for an average pyrolysis tar residence time in the reactor of at least 120 seconds (e.g., at least 160 seconds), R_{Ref} is typically $\leq 5 \times 10^{19}$ spins per gram of the pyrolysis tar. For example, R_{Ref} can be $\leq 1 \times 10^{19}$ spins per gram of the pyrolysis tar, such as $\leq 5 \times 10^{18}$ spins per gram of the pyrolysis tar, or $\leq 2 \times 10^{18}$ spins per gram of the pyrolysis tar, or $\leq 1 \times 10^{18}$ spins per gram of the pyrolysis tar. R_{Ref} can also be expressed in BN. Under the selected conditions, R_{Ref} is typically ≤ 20 BN, e.g., ≤ 18 BN, such as ≤ 12 BN, or ≤ 10 BN, or ≤ 8 BN.

Comparing R_T and R_{Ref}

[0057] In certain aspects, R_T is compared with a pre-determined R_{Ref} as follows. A reference reactivity R_{Ref} is pre-determined, as specified for the desired hydroprocessing conditions. A pyrolysis tar sample is taken as specified, and the reactivity R_T of the sample is
5 determined (e.g., using one or more of BN, ESR, etc.). If R_T is $\leq R_{Ref}$, the sampled tar (e.g., at least a portion of the tar that remains after the sample is removed) can be conducted as pyrolysis tar feed to a hydroprocessing stage for hydroprocessing under Standard Hydroprocessing Conditions in the presence of the specified utility fluid.

[0058] If R_T exceeds R_{Ref} , the sampled tar or a portion thereof can be stored and/or
10 further processed, e.g., by one or more of (i) conducting away the sampled tar without hydroprocessing; (ii) hydroprocessing the sampled tar under Mild Hydroprocessing Conditions in the presence of the specified utility fluid; and (iii) treating the sampled tar (e.g., by the specified blending and/or thermal treatments) to produce a treated tar.

[0059] A treated tar can be re-sampled for an R_T measurement. If R_T of the treated tar
15 does not exceed R_{Ref} , the treated tar or a portion thereof can be conducted to the specified hydroprocessing stage for hydroprocessing under Standard Hydroprocessing Conditions in the presence of the specified utility fluid. Should R_T of the treated tar still exceed R_{Ref} , one or more re-treatments can be carried out, e.g., one or more additional blending and/or thermal treatments, to produce a re-treated tar. The re-treated tar is then re-tested for reactivity. The
20 specified treatments and re-treatments can be carried out until a sample of the treated (or re-treated) tar has an R_T that does not exceed R_{Ref} by a desired amount (e.g., $R_T \leq 25\%$ of R_{Ref}), or until further re-treatments are not warranted, as may be the case these would not result in an economic or processing benefit. A treated or re-treated tar (namely a pyrolysis tar composition) having an $R_T > R_{Ref}$ can be processed by one or more of (i) storing for later
25 processing or use; (ii) conducting away without hydroprocessing; and (iii) hydroprocessing under Mild Hydroprocessing Conditions in the presence of the specified utility fluid.

Treating or Re-Treating a Pyrolysis Tar by Blending

[0060] A sampled pyrolysis tar having an $R_T > R_{Ref}$ can be treated or re-treated by
blending to produce a blended tar that is suitable for use as a pyrolysis tar feed, e.g., a
30 blended tar having an $R_T \leq R_{Ref}$. Blending can be carried out by combining the sampled tar with a sufficient amount of at least a second pyrolysis tar having an $R_T < R_{Ref}$ to achieve a blend R_T that does not exceed R_{Ref} by a desired amount, e.g., $R_T \leq 25\%$ of R_{Ref} , such as $R_T \leq 10\%$ of R_{Ref} . For example, one or more of R_T of the first pyrolysis tar, R_T of the second pyrolysis tar, and R_T of the blend can each be determined by ESR.

[0061] Alternatively or in addition, BN measurements can be used to determine one or more of R_T of the first pyrolysis tar, R_T of the second pyrolysis tar, and R_T of the blend. For example, a plurality of pyrolysis tars, including a plurality of SCTs, may be blended to produce a blended pyrolysis tar with a specific aliphatic olefin content, e.g., one exhibiting a
 5 blended sample $R_T \leq R_{Ref}$ as measured by BN. A blended tar having an $R_T \leq R_{Ref}$ can be conducted to a hydroprocessing stage as pyrolysis tar feed for hydroprocessing under Standard Hydroprocessing Conditions in the presence of the specified utility fluid. If the blended tar's R_T exceeds R_{Ref} , it can be stored for later processing and/or use; re-treated, e.g., by the specified thermal treatment and/or additional blending; and/or hydroprocessed under
 10 Mild Hydroprocessing Conditions in the presence of the specified utility fluid.

[0062] Although it is typical to directly measure the blend's R_T , this is not required, and in some aspects a calculated value of the blend's R_T is used. The calculation is based on the observation that pyrolysis tar reactivity (e.g., as measured by ESR, BN, etc.) is substantially stable for typical blending time durations (e.g., in a range of about one minute to about 24
 15 hours) at a substantially constant temperature. Accordingly, a blend's R_T can be estimated from the reactivities of the first and second pyrolysis tars used to produce the blend (R_{T1} and R_{T2}) using the formula:

$$R_{Tblend} \sim \{(R_{T1} * \text{grams tar 1}) + (R_{T2} * \text{grams tar 2})\} / (\text{grams tar 1} + \text{grams tar 2}).$$

[0063] In certain aspects, an R_{Ref} is pre-determined, e.g., before a comparison with R_T ,
 20 using one or more of the specified R_{Ref} determination methods. For example, an R_{Ref} substantially equal to 2×10^{18} spins per gram can be established by ESR measurements for hydroprocessing carried out under Standard Hydroprocessing Conditions including a temperature $\geq 480^\circ\text{C}$ and a residence time ≥ 120 seconds. A first SCT (SCT1) is evaluated for suitability as pyrolysis tar feed by measuring R_T using one or more of the specified R_T
 25 determination methods, e.g., ESR and/or BN. If R_T of SCT1 is $\leq R_{Ref}$, no alteration or blending of SCT1 is indicated before hydroprocessing. If however R_T of SCT 1 is $> R_{Ref}$, fouling potential is lessened by blending SCT1 with a second SCT (SCT2), where R_T of SCT2 is $< R_{Ref}$. For instance, if R_T of SCT1 is about 1×10^{19} spins per gram, and R_T of SCT2 is about 5×10^{17} spins per gram, then a blend of 100 grams of SCT1 with about 500 grams of
 30 SCT2. (e.g., using a blend ratio of (wt. % SCT2 in blend / wt. % SCT1 in blend) $\sim 83.6/16.6$, or ~ 5.0) is estimated to produce a blended SCT with an estimated R_T for the blend of about 2×10^{18} spins/gram. As another example, if R_T of SCT1 is about 30 (BN), and R_T of SCT2 is about 24 (BN), then a blend of 200 grams of SCT1 with about 200 grams of SCT2. (e.g.,

using a blend ratio of (wt. % SCT2 in blend / wt. % SCT 1 in blend) is estimated to produce a blended SCT having an R_T for the blend of about 27 BN.

[0064] If a blended sample's reactivity R_T is still greater than R_{Ref} , then (i) the blend ratio may be increased to produce a re-blended tar having a lesser R_T and/or (ii) one or more additional pyrolysis tars having an R_T that is less than or equal to that of SCT2 can be added to the blend. R_T of the re-blended tar can be measured using any of the specified methods for measuring R_T .

[0065] Blending of pyrolysis tar can cause precipitation or particulates, particularly when the pyrolysis tar has an $I_N > 110$. Precipitation of particulates (e.g., asphaltenes) during and after blending is lessened when the first pyrolysis tar (which may itself be a mixture of pyrolysis tars) has an $S_{BN} > 135$ and an $I_N > 80$ and the S_{BN} of the blended tar composition is at least 20 solvency units greater than the second pyrolysis tar's (and/or the blended pyrolysis tar's) I_N . For example, it can be desirable to carry out blending such that (i) the first pyrolysis tar has an $S_{BN} > 135$ and an $I_N > 80$, (ii) the second pyrolysis tar has an S_{BN} that is less than that of the first pyrolysis tar, (iii) the blended tar composition has an S_{BN} that is less than that of the first pyrolysis tar, (iv) the second pyrolysis tar (and/or the blend) has an I_N that is less than that of the first pyrolysis tar, and (v) the S_{BN} of the blended tar composition is at least 20 solvency units greater than the second pyrolysis tar's I_N , or more preferred, at least 30 solvency units, or most preferred, at least 40 solvency units greater than the second pyrolysis tar's I_N . Optionally, the second tar's (or any additional tar's) I_N is less than the S_{BN} of the final pyrolysis tar blend. Parameters S_{BN} and I_N can be determined using the methods disclosed in U.S. Patent No. 5,871,634.

Treating or Re-Treating a Pyrolysis Tar by Thermal Treatment

[0066] As an alternative or in addition to blending, a sampled tar's R_T can be decreased (e.g., improved) by one or more thermal treatments. Conventional thermal treatments are suitable, including heat soaking, but the invention is not limited thereto. One or more of such thermal treatments can be used instead of or in addition to blending of the sampled tar with additional pyrolysis tar. It is believed that the specified thermal treatment is particularly effective for decreasing the tar's aliphatic olefin content.

[0067] One representative pyrolysis tar is an SCT having an $R_T > R_{Ref}$ (e.g., an $R_T \geq 28$ BN), a density at 15°C that is ≥ 1.10 g/cm³, a 50°C viscosity in the range of $\geq 1.0 \times 10^4$ cSt, an $I_N > 80$, wherein ≥ 70 wt. % of the pyrolysis tar's hydrocarbon have an atmospheric boiling point of $\geq 290^\circ\text{C}$. This pyrolysis tar can be provided, e.g., as a tar stream entering a tar drum located downstream of steam cracker effluent quenching. When this SCT is

provided at a temperature T_1 in the range of about 140°C to 350°C, the thermal treatment can include heating the SCT to a temperature T_{HS} that is at least 10°C greater than T_1 , e.g., at least 20°C greater than T_1 , such as 30°C greater than T_1 . The heating can be carried out in a lower section of the tar drum, e.g., by introducing steam (which also desirably strips from the tar any lighter hydrocarbon as may be present). The heated SCT is then maintained within a temperature range that is $\geq T_{HS}$ and $\leq 360^\circ\text{C}$ for a time t_{HS} in the range of from 1 minute to 400 minutes. In certain aspects, the thermal treatment conditions include (i) T_{HS} is at least 10°C greater than T_1 and (ii) T_{HS} is in the range of 300°C to 360°C. Typical T_{HS} and t_{HS} ranges include $180^\circ\text{C} \leq T_{HS} \leq 320^\circ\text{C}$ and $5 \text{ minutes} \leq t_{HS} \leq 100 \text{ minutes}$; e.g., $200^\circ\text{C} \leq T_{HS} \leq 280^\circ\text{C}$ and $5 \text{ minute} \leq t_{HS} \leq 30 \text{ minutes}$. The specified thermal treatment is effective for decreasing the representative SCT's R_T into a range of $R_T \leq 0.9 \cdot R_{Ref}$, such as an $R_T \leq 0.75 \cdot R_{Ref}$, or an $R_T \leq 0.5 \cdot R_{Ref}$, or e.g., $R_T \leq 0.1 \cdot R_{Ref}$. For example, thermally treating a representative pyrolysis tar having an $R_T \geq 28 \text{ BN}$ as specified has been found to produce a treated tar having an R_T that is typically $\leq 20 \text{ BN}$, e.g., $\leq 18 \text{ BN}$, such as $\leq 12 \text{ BN}$, or $\leq 10 \text{ BN}$, or $\leq 8 \text{ BN}$.

[0068] When the thermal treatment includes heat soaking, the heat soaking can be carried out at least in part in one or more soaker drums and/or in vessels, conduits, and other equipment (e.g. flash drums, knock out drums, fractionators, water-quench towers, indirect condensers) associated with, e.g., (i) separating the pyrolysis tar from the pyrolysis effluent and/or (ii) conveying the pyrolysis tar to hydroprocessing. The location of the thermal treatment is not critical. The thermal treatment can be carried out at any convenient location, e.g., after tar separation from the pyrolysis effluent and before hydroprocessing, such as downstream of a tar drum and upstream of mixing the thermally treated tar with utility fluid.

[0069] In certain aspects, the pyrolysis tar subjected to thermal treatment comprises SCT or a blend comprising SCT. At least part of the thermal treatment can be carried out in one or more tar drums and/or a steam cracker primary fractionator, e.g., by regulating a bottoms pump-around loop in the drum and/or fractionator to achieve the specified thermal treatment conditions. For instance, in the processing illustrated schematically in Fig. 1, pyrolysis tar in conduit 63 is piped via line 65 to for mixing with a utility fluid supplied via line 310. Piping 65 can be insulated to maintain the temperature of pyrolysis tar within the desired temperature range for the desired residence time prior mixing with the utility fluid from line 10.

[0070] Alternatively or in addition, other process equipment (existing or added) can be used for the thermal treatment, such as one or more heat exchangers for heating the tar to

achieve the specified T_{HS} for the specified t_{HS} . More than one heat exchanger can be used: a first heat exchanger may be positioned before or after pump 64 for an indirect transfer of heat to the SCT, with a second heat exchanger positioned at a location along line 65. The first heat exchanger operates by indirectly transferring heat to the tar from a first working fluid which enters the first heat exchanger at a temperature greater than that at which the tar enters. The second heat exchanger removes heat from the heated tar in order to decrease the tar's temperature to below 150°C (which substantially halts heat soaking) after the desired t_{HS} has been achieved. The second heat exchanger operates by transferring heat from the heated tar to a second working fluid, which enters the second heat exchanger at a temperature less than that at which the heated tar enters. For instance, it may be desired to heat soak an SCT stream that is removed from a separation drum, the removed tar having a temperature T_1 in the range of 240°C to 290°C. A first heat exchanger can be located along conduit 65 to increase the SCT's temperature to the desired heat soak temperature T_{HS} for the desired heat soak time t_{HS} . For example, T_{HS} can be at least 10°C greater than T_1 and less than 360°C, e.g., in the range of about 250°C (when T_1 is 240°C) to 360°C, such as 275°C to 325°C (when $265^\circ\text{C} \leq T_1 \leq 315^\circ\text{C}$). The heat soak time t_{HS} can be, e.g., ≥ 10 minutes, such as in the range of from 10 minutes to 30 minutes. Typically, the tar is heated in the first heat exchanger to a temperature that typically is slightly greater (e.g., about 10°C greater) than the desired T_{HS} to allow for heat losses in conduit 65 during transit. In aspects where (i) the desired t_{HS} is in the range of from 15 minutes to 25 minutes and (ii) the heated tar's residence time in conduit 65 exceeds 25 minutes, a second heat exchanger may be located along conduit 65 that is about 25 minutes' downstream of the first heat exchanger, where the second heat exchanger cools the heated tar to a temperature of 150°C or less. In aspects exhibiting a substantially constant tar flow rate, the heat exchangers can be adjusted to produce an SCT temperature substantially equal to the desired T_{HS} at a location along conduit 65 that is about midway between the first and second exchangers.

[0071] The comparison of R_{Ref} with a treated or re-treated tar's R_T can be carried out in substantially the same way as described for the sampled tar. Options available for processing the treated or re-treated tar based on the results of the comparison of R_T and R_{Ref} are substantially the same as those available for the sampled tar. In other words, if the treated or re-treated tar's R_T exceeds R_{Ref} , it can be one or more of (i) stored for later processing and/or use; (ii) subjected to additional treatments, e.g., by additional thermal treatment and/or additional blending; and (iii) hydroprocessing under Mild Hydroprocessing Conditions in the presence of the specified utility fluid. A treated or re-treated tar having an $R_T \leq R_{Ref}$ can be

conducted to a hydroprocessing stage as pyrolysis tar feed for hydroprocessing under Standard Hydroprocessing Conditions in the presence of the specified utility fluid. A further decrease in fouling potential can be obtained by carrying out the treating to achieve an R_T of the treated tar that is equal to R_{Ref} , e.g., by further increasing the blend ratio. For example, 5 treating or re-treating (such as additional blending and/or additional heat soaking) can be used to achieve an $R_T \leq 0.9 * R_{Ref}$, such as an $R_T \leq 0.75 * R_{Ref}$, or an $R_T \leq 0.5 * R_{Ref}$, or e.g., $R_T \leq 0.1 * R_{Ref}$, or $R_T \leq 18 \text{ BN}$, e.g., $\leq 12 \text{ BN}$, such as $\leq 10 \text{ BN}$, or $\leq 8 \text{ BN}$.

[0072] The pyrolysis tar feed typically comprises $\geq 50 \text{ wt. \%}$ of pyrolysis tar, such as SCT, e.g., $\geq 75 \text{ wt. \%}$, such as $\geq 90 \text{ wt. \%}$. In certain aspects, the pyrolysis tar feed is 10 substantially all pyrolysis tar. At least part of the hydroprocessing of the pyrolysis tar feed is carried out in the presence of a utility fluid. Certain forms of utility fluid will now be described in more detail. The invention is not limited to these forms, and this description is not meant to foreclose using other utility fluids within the broader scope of the invention.

Utility Fluids

15 [0073] Depending on processing options indicated by the outcome of the R_T vs. R_{Ref} comparison, a pyrolysis tar feed may be hydroprocessed in one or more hydroprocessor stages. At least one stage of the hydroprocessing is carried out in the presence of a utility fluid comprising 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 20 utility fluid can contain ring compounds in an amount $\geq 40.0 \text{ wt. \%}$, $\geq 45.0 \text{ wt. \%}$, $\geq 50.0 \text{ wt. \%}$, $\geq 55.0 \text{ wt. \%}$, or $\geq 60.0 \text{ wt. \%}$, based on the weight of the utility fluid. In certain aspects, at least a portion of the utility fluid is obtained from the hydroprocessor effluent, e.g., by one or more separations. This can be carried out as disclosed in U.S. Patent No. 9,090,836, which is incorporated by reference herein in its entirety.

25 [0074] Typically, the utility fluid comprises aromatic hydrocarbon, e.g., $\geq 25.0 \text{ wt. \%}$, such as $\geq 40.0 \text{ wt. \%}$, or $\geq 50.0 \text{ wt. \%}$, or $\geq 55.0 \text{ wt. \%}$, or $\geq 60.0 \text{ wt. \%}$ of aromatic hydrocarbon, based on the weight of the utility fluid. The aromatic hydrocarbon can include, e.g., one, two, and three ring aromatic hydrocarbon compounds. For example, the utility fluid can comprise $\geq 15 \text{ wt. \%}$ of 2-ring and/or 3-ring aromatics, based on the weight of the 30 utility fluid, such as $\geq 20 \text{ wt. \%}$, or $\geq 25.0 \text{ wt. \%}$, or $\geq 40.0 \text{ wt. \%}$, or $\geq 50.0 \text{ wt. \%}$, or $\geq 55.0 \text{ wt. \%}$, or $\geq 60.0 \text{ wt. \%}$. Utilizing a utility fluid comprising aromatic hydrocarbon compounds having 2-rings and/or 3-rings is advantageous because utility fluids containing these compounds typically exhibit an appreciable S_{BN} .

[0075] The utility fluid typically has an A.S.T.M. D86 10% distillation point $\geq 60^{\circ}\text{C}$ and a 90% distillation point $\leq 425^{\circ}\text{C}$, e.g., $\leq 400^{\circ}\text{C}$. In certain aspects, the utility fluid has a true boiling point distribution with an initial boiling point $\geq 130^{\circ}\text{C}$ (266°F) and a final boiling point $\leq 566^{\circ}\text{C}$ (1050°F). In other aspects, the utility fluid has a true boiling point distribution with an initial boiling point $\geq 150^{\circ}\text{C}$ (300°F) and a final boiling point $\leq 430^{\circ}\text{C}$ (806°F). In still other aspects, the utility has a true boiling point distribution with an initial boiling point $\geq 177^{\circ}\text{C}$ (350°F) and a final boiling point $\leq 425^{\circ}\text{C}$ (797°F). True boiling point distributions (the distribution at atmospheric pressure) can be determined, e.g., by conventional methods such as the method of A.S.T.M. D7500. When the final boiling point is greater than that specified in the standard, the true boiling point distribution can be determined by extrapolation. A particular form of the utility fluid has a true boiling point distribution having an initial boiling point $\geq 130^{\circ}\text{C}$ and a final boiling point $\leq 566^{\circ}\text{C}$; and/or comprises ≥ 15 wt. % of two ring and/or three ring aromatic compounds.

[0076] The amounts of utility fluid and pyrolysis tar feed employed during hydroprocessing are generally in the range of from about 20.0 wt. % to about 95.0 wt. % of the pyrolysis tar feed and from about 5.0 wt. % to about 80.0 wt. % of the utility fluid, based on total weight of utility fluid plus pyrolysis tar feed. For example, the relative amounts of utility fluid and pyrolysis tar feed during hydroprocessing can be in the range of (i) about 20.0 wt. % to about 90.0 wt. % of the pyrolysis tar feed and about 10.0 wt. % to about 80.0 wt. % of the utility fluid, or (ii) from about 40.0 wt. % to about 90.0 wt. % of the pyrolysis tar feed and from about 10.0 wt. % to about 60.0 wt. % of the utility fluid. The utility fluid : pyrolysis tar feed weight ratio is typically ≥ 0.01 , e.g., in the range of 0.05 to 4.0, such as in the range of 0.1 to 3.0, or 0.3 to 1.1. At least a portion of the utility fluid can be combined with at least a portion of the pyrolysis tar feed during the hydroprocessing, e.g., within a hydroprocessing zone, but this is not required. In certain aspects, at least a portion of the utility fluid and at least a portion of the pyrolysis tar feed are supplied as separate streams and combined into one feed stream (the "hydroprocessor feed") prior to entering (e.g., upstream of) the hydroprocessing stage(s). For example, the pyrolysis tar feed and utility fluid can be combined to produce a hydroprocessor feed upstream of the hydroprocessing stage, the hydroprocessor feed comprising, e.g., (i) about 20.0 wt. % to about 90.0 wt. % of the pyrolysis tar feed and about 10.0 wt. % to about 80.0 wt. % of the utility fluid, or (ii) from about 40.0 wt. % to about 90.0 wt. % of the pyrolysis tar feed and from about 10.0 wt. % to about 60.0 wt. % of the utility fluid, the weight percents being based on the weight of the hydroprocessor feed.

[0077] In certain aspects, the pyrolysis tar feed is combined with a utility fluid to produce a hydroprocessor feed. Typically these aspects feature one or more of (i) a utility fluid having an $S_{BN} \geq 100$, e.g., $S_{BN} \geq 110$; a pyrolysis tar feed having an $I_N > 70$, e.g., > 80 ; and (iii) > 70 wt. % of the pyrolysis tar feed resides in compositions having an atmospheric boiling point $\geq 290^\circ\text{C}$. The hydroprocessor feed can have, e.g., an $S_{BN} \geq 110$, such as ≥ 120 , or ≥ 130 . It has been found that there is a beneficial decrease in reactor plugging when hydroprocessing pyrolysis tars an $I_N > 110$ provided that, after being combined with the utility fluid, the hydroprocessor feed has an $S_{BN} \geq 150$, ≥ 155 , or ≥ 160 . The pyrolysis tar (or mixture of pyrolysis tars) can have a relatively large insolubility number, e.g., $I_N > 80$, especially > 100 , or > 110 , provided the utility fluid has relatively large S_{BN} , e.g., $S_{BN} \geq 100$, ≥ 120 , or ≥ 140 .

[0078] Certain aspects of the invention will now be described in which a pyrolysis tar feed is hydroprocessed under the specified hydroprocessing conditions (Standard Hydroprocessing Conditions or Mild Hydroprocessing Conditions, as the case may be) to produce a hydroprocessed pyrolysis tar. The invention is not limited to these aspects, and this description is not meant to foreclose other aspects within the broader scope of the invention.

Hydroprocessing

[0079] The pyrolysis tar feed is typically combined with utility fluid to produce a hydroprocessor feed before hydroprocessing. The hydroprocessor feed is hydroprocessed in the presence of a treatment gas comprising molecular hydrogen, and generally in the presence of at least one catalyst. The hydroprocessing produces a hydroprocessed pyrolysis tar product (the hydroprocessed pyrolysis tar) that typically exhibits one or more of a decreased viscosity, decreased atmospheric boiling point range, and increased hydrogen content over that of the pyrolysis tar feed. These features lead in turn to improved compatibility of the tar with other heavy oil blendstocks, and improved utility as a fuel oil and blend-stock.

[0080] Depending on processing options indicated by the comparison of R_{Ref} and the pyrolysis tar feed's R_T , the hydroprocessing is carried out under Standard Hydroprocessing Conditions or Mild Hydroprocessing Conditions. The name by which the hydroprocessing is identified is not critical. For example, the hydroprocessing can be characterized as or more of hydrocracking (including selective hydrocracking), hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, hydrodearomatization, hydroisomerization, or hydrodewaxing. The hydroprocessing can be carried out in at least one vessel or zone that is located, e.g., within a hydroprocessing stage downstream of the

pyrolysis stage and the stage or stages within which the hydroprocessed tar is recovered. Typically, the hydroprocessing temperatures in a hydroprocessing zone is the average temperature of the hydroprocessing reactor's catalyst bed (one half the difference between the bed's inlet and outlet temperature). When the hydroprocessing reactor contains more than
5 one hydroprocessing zone and/or more than one catalyst bed (e.g., as shown in Fig. 1) the hydroprocessing temperature is the average temperature in the hydroprocessing reactor, e.g., (one half the difference between the temperature of the most upstream catalyst bed's inlet and the temperature of the most downstream catalyst bed's outlet temperature).

[0081] Hydroprocessing is carried out in the presence of hydrogen, e.g., by (i) combining
10 molecular hydrogen with the pyrolysis tar feed and/or utility fluid upstream of the hydroprocessing, and/or (ii) conducting molecular hydrogen to the hydroprocessing stage in one or more conduits or lines. Although relatively pure 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.,
15 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 optionally contains $\geq$ about 50 vol. % of molecular hydrogen, e.g., $\geq$ about 75 vol. %, based on the total volume of treat gas conducted to the hydroprocessing stage.

[0082] The pyrolysis tar feed can be upgraded before it is combined with the utility fluid
20 to produce the hydroprocessor feed. For example, Fig. 1 schematically shows a pyrolysis tar feed introduced via conduit 61 to separation stage 62 for separation of one or more light gases and/or particulates from the pyrolysis tar feed. An upgraded pyrolysis tar feed is collected in conduit 63 and transferred by pump 64 through conduit 65. The upgraded pyrolysis tar feed is combined with a utility fluid supplied via line 310 to produce the hydroprocessor feed,
25 which is conducted to a first pre-heater 70 via conduit 320. Optionally, a supplemental utility fluid, may be added via conduit 330. The hydroprocessor feed (which typically is primarily in liquid phase) is conducted to a supplemental pre-heat stage 90 via conduit 370. The supplemental pre-heat stage 90 can be, e.g., a fired heater. Recycled treat gas, comprising molecular hydrogen, is obtained from conduit 265 and, if necessary, is mixed with fresh treat
30 gas, supplied through conduit 131. The treat gas is conducted via conduit 60 to a second pre-heater 360, before being conducted to the supplemental pre-heat stage 90 via conduit 80. Fouling in reactor 110 can be decreased by increasing pyrolysis tar pre-heater duty in pre-heaters 70 and 90. It has surprisingly been found that when $R_T \leq R_{Ref}$ that pyrolysis tar pre-heater duty can be decreased. Even more surprisingly, it has been found that for a

pyrolysis tar having an $R_T \leq 18$ BN, e.g., ≤ 12 BN, such as ≤ 10 BN, or ≤ 8 BN (as can be achieved by one or more of the specified treatments, e.g., one or more of the specified blendings or thermal treatments), that it is not necessary to carry out a mild hydroprocessing of the treated tar before hydroprocessing under Standard Hydroprocessing Conditions.

5 Beneficially, this is the case even for a pyrolysis tar having an initial R_T (before treatment) that is > 28 .

[0083] The pre-heated hydroprocessor feed (from line 380) is combined with the pre-heated treat gas (from line 390) and then conducted via line 100 to a hydroprocessing reactor 110. Mixing means can be utilized for combining the pre-heated hydroprocessor feed with
10 the pre-heated treat gas in hydroprocessing reactor 110, e.g., one or more gas-liquid distributors of the type conventionally utilized in fixed bed reactors. The hydroprocessing is carried out in the presence of a catalytically effective amount of at least one hydroprocessing catalyst located in at least one catalyst bed 115. Additional catalyst beds, e.g., 116, 117, etc., may be connected in series with the catalyst bed 115 with optional intercooling quench using
15 treat gas from conduit 60 being provided between beds (not shown).

[0084] A hydroprocessor effluent is conducted away from hydroprocessing reactor 110 via conduit 120. When the second and third preheaters (360 and 70) are heat exchangers, the hot hydroprocessing effluent in conduit 120 can be used to preheat the tar/utility fluid and the treat gas respectively by indirect heat transfer. Following this optional heat exchange, the
20 hydroprocessor effluent is conducted to separation stage 130 for separating total vapor product (e.g., heteroatom vapor, vapor-phase cracked products, unused treat gas, etc.) and total liquid product ("TLP") from the hydroprocessed effluent. The total vapor product is conducted via line 200 to upgrading stage 220, which comprises, e.g., one or more amine towers. Fresh amine is conducted to stage 220 via line 230, with rich amine conducted away
25 via line 240. Unused treat gas is conducted away from stage 220 via line 250, compressed in compressor 260, and conducted via lines 265, 60, and 80 for re-cycle and re-use in the hydroprocessing stage 110.

[0085] The TLP from separation stage 130 typically comprises hydroprocessed pyrolysis tar, e.g., ≥ 10 wt. % of hydroprocessed pyrolysis tar, such as ≥ 50 wt. %, or ≥ 75 wt. %, or $\geq$
30 90 wt. %. The TLP optionally contains non-tar components, e.g., hydrocarbon having a true boiling point range that is substantially the same as that of the utility fluid (e.g., unreacted utility fluid). The TLP, which is an upgraded tar product, is useful as a diluent (e.g., a flux) for heavy hydrocarbons, especially those of relatively high viscosity. Optionally, all or a portion of the TLP can substitute for more expensive, conventional diluents. Non-limiting

examples of heavy, high-viscosity streams suitable for blending with the bottoms include one or more of bunker fuel, burner oil, heavy fuel oil (e.g., No. 5 or No. 6 fuel oil), high-sulfur fuel oil, low-sulfur fuel oil, regular-sulfur fuel oil (RSFO), and the like.

[0086] In the aspects illustrated in Fig. 1, TLP from separation stage 130 is conducted via line 270 to a further separation stage 280, e.g., for separating from the TLP one or more of hydroprocessed pyrolysis tar, additional vapor, and at last one stream suitable for use as recycle as utility fluid or a utility fluid component. Separation stage 280 may be, for example, a distillation column with side-stream draw although other conventional separation methods may be utilized. The TLP is separated in further separation stage 280 into an overhead stream, a side stream and a bottoms stream, listed in order of increasing boiling point. The overhead stream (e.g., vapor) is conducted away from separation stage 280 via line 290. The bottoms stream (typically comprising a major amount of the hydroprocessed pyrolysis tar) is conducted away via line 134. At least a portion of the overhead and bottoms streams may be conducted away, e.g., for storage and/or for further processing. The bottoms portion of the TLP can be desirable as a diluent (e.g., a flux) for heavy hydrocarbon, e.g., heavy fuel oil. In certain aspects, at least a portion of the overhead stream 290 is combined with at least a portion of the bottoms stream 134 to form an upgraded tar product (not shown).

[0087] Optionally, the operation of separation stage 280 is adjusted to shift the boiling point distribution of side stream 340 so that side stream 340 has properties desired for the utility fluid, e.g., (i) a true boiling point distribution having an initial boiling point $\geq 177^{\circ}\text{C}$ (350°F) and a final boiling point $\leq 566^{\circ}\text{C}$ (1050°F) and/or (ii) an $S_{\text{BN}} \geq 100$, e.g., ≥ 120 , such as ≥ 125 , or ≥ 130 . Optionally, trim molecules may be separated, for example, in a fractionator (not shown), from separation stage 280 bottoms or overhead or both and added to the side stream 340 as desired. The side stream is conducted away from separation stage 280 via conduit 340. At least a portion of the side stream 340 can be utilized as utility fluid and conducted via pump 300 and conduit 310. Typically, the side stream composition of line 310 is at least 10 wt. % of the utility fluid, e.g., ≥ 25 wt. %, such as ≥ 50 wt. %.

[0088] Conventional hydroprocessing catalysts can be utilized for hydroprocessing the pyrolysis tar stream in the presence of the utility fluid, such as those specified for use in resid and/or heavy oil hydroprocessing, but the invention is not limited thereto. Suitable hydroprocessing catalysts include bulk metallic catalysts and supported catalysts. The metals can be in elemental form or in the form of a compound. Typically, the hydroprocessing catalyst includes at least one metal from any of Groups 5 to 10 of the

Periodic Table of the Elements (tabulated as the Periodic Chart of the Elements, The Merck Index, Merck & Co., Inc., 1996). Examples of such catalytic metals include, but are not limited to, vanadium, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, cobalt, nickel, ruthenium, palladium, rhodium, osmium, iridium, platinum, or mixtures thereof. Suitable conventional catalysts include one or more of KF860 available from Albemarle Catalysts Company LP, Houston TX; Nebula[®] Catalyst, such as Nebula[®] 20, available from the same source; Centera[®] catalyst, available from Criterion Catalysts and Technologies, Houston TX, such as one or more of DC-2618, DN-2630, DC-2635, and DN-3636; Ascent[®] Catalyst, available from the same source, such as one or more of DC-2532, DC-2534, and DN-3531; and FCC pre-treat catalyst, such as DN3651 and/or DN3551, available from the same source.

[0089] In certain aspects, the catalyst has a total amount of Groups 5 to 10 metals per gram of catalyst of at least 0.0001 grams, or at least 0.001 grams or at least 0.01 grams, in which grams are calculated on an elemental basis. For example, the catalyst can comprise a total amount of Group 5 to 10 metals in a range of from 0.0001 grams to 0.6 grams, or from 0.001 grams to 0.3 grams, or from 0.005 grams to 0.1 grams, or from 0.01 grams to 0.08 grams. In particular aspects, the catalyst further comprises at least one Group 15 element. An example of a preferred Group 15 element is phosphorus. When a Group 15 element is utilized, the catalyst can include a total amount of elements of Group 15 in a range of from 0.000001 grams to 0.1 grams, or from 0.00001 grams to 0.06 grams, or from 0.00005 grams to 0.03 grams, or from 0.0001 grams to 0.001 grams, in which grams are calculated on an elemental basis.

[0090] Hydroprocessing is carried out under Standard or Mild Hydroprocessing Conditions depending on processing options indicated by the comparison of R_T and R_{Ref} . These conditions will now be described in more detail.

Standard Hydroprocessing Conditions

[0091] Standard Hydroprocessing Conditions include a temperature $\geq 200^\circ\text{C}$, a pressure ≥ 8 MPa, and a weight hourly space velocity (“WHSV”) of the pyrolysis tar feed that is ≥ 0.3 hr^{-1} . Optionally, the Standard Hydroprocessing Conditions include a temperature $> 400^\circ\text{C}$, e.g., in the range of from 300°C to 500°C , such as 350°C to 430°C , or 350°C to 420°C , or 360°C to 420°C ; and a WHSV in the range of from 0.3 hr^{-1} to 20 hr^{-1} or 0.3 hr^{-1} to 10 hr^{-1} . Typically, Standard Hydroprocessing Conditions include a molecular hydrogen partial pressure during the hydroprocessing that is generally ≥ 8 MPa, such ≥ 9 MPa, or ≥ 10 MPa, although in certain aspects it is ≤ 14 MPa, such as ≤ 13 MPa, or ≤ 12 MPa. WHSV of the

pyrolysis tar feed is optionally $\geq 0.5 \text{ hr}^{-1}$, e.g., in the range of from 0.5 hr^{-1} to 20 hr^{-1} , such as 0.5 hr^{-1} to 10 hr^{-1} . WHSV of the hydroprocessor feed (the pyrolysis tar feed combined with utility fluid) is typically $\geq 0.5 \text{ hr}^{-1}$, such as $\geq 1.0 \text{ hr}^{-1}$, although in certain aspects it is $\leq 5 \text{ hr}^{-1}$, such as $\leq 4 \text{ hr}^{-1}$, for example $\leq 3 \text{ hr}^{-1}$.

- 5 **[0092]** The amount of molecular hydrogen supplied to a hydroprocessing stage operating under Standard Hydroprocessing Conditions is typically in the range of from about 1000 SCF/B (standard cubic feet per barrel) ($178 \text{ S m}^3/\text{m}^3$) to 10000 SCF/B ($1780 \text{ S m}^3/\text{m}^3$), in which B refers to barrel of hydroprocessor feed to the hydroprocessing stage (the pyrolysis tar feed combined with the utility fluid). For example, the molecular hydrogen can be
- 10 provided in a range of from 3000 SCF/B ($534 \text{ S m}^3/\text{m}^3$) to 6000 SCF/B ($1068 \text{ S m}^3/\text{m}^3$). In another aspect, the rate can be $270 \text{ (S m}^3/\text{m}^3)$ of molecular hydrogen per cubic meter of the pyrolysis tar feed to $534 \text{ S m}^3/\text{m}^3$. The amount of molecular hydrogen supplied to hydroprocess the pyrolysis tar feed is typically less than would be the case if the pyrolysis tar feed contained greater amounts of aliphatic olefin, e.g., C_{6+} olefin, such as vinyl aromatics.
- 15 The molecular hydrogen consumption rate during Standard Hydroprocessing Conditions is typically in the range of about 270 standard cubic meters/cubic meter ($\text{S m}^3/\text{m}^3$) to about 534 $\text{S m}^3/\text{m}^3$ (1520 SCF/B to 3000 SCF/B , where the denominator represents barrels of the pyrolysis tar feed, e.g., barrels of SCT in a hydroprocessor feed, e.g., in the range of about 280 to about $430 \text{ S m}^3/\text{m}^3$, such as about 290 to about $420 \text{ S m}^3/\text{m}^3$, or about 300 to about 410
- 20 $\text{S m}^3/\text{m}^3$. The indicated molecular hydrogen consumption rate is typical for a pyrolysis tar feed containing $\leq 5 \text{ wt. \%}$ of sulfur, e.g., $\leq 5 \text{ wt. \%}$, such as $\leq 1 \text{ wt. \%}$, or $\leq 0.5 \text{ wt. \%}$. A greater amount of molecular hydrogen is typically consumed when the pyrolysis tar feed contains a greater sulfur amount.

- [0093]** Within the parameter ranges (T, P, WHSV, etc.) specified for Standard
- 25 Hydroprocessing Conditions, particular hydroprocessing conditions for a particular pyrolysis tar feed are typically selected to (i) achieve the desired $566^\circ\text{C}+$ conversion, typically $\geq 20 \text{ wt. \%}$ substantially continuously for at least ten days, and (ii) produce a TLP and hydroprocessed pyrolysis tar having the desired properties, e.g., the desired density and viscosity. The term $566^\circ\text{C}+$ conversion means the conversion during hydroprocessing of pyrolysis tar compounds
- 30 having boiling a normal boiling point $\geq 566^\circ\text{C}$ to compounds having boiling points $< 566^\circ\text{C}$. This $566^\circ\text{C}+$ conversion includes a high rate of conversion of THs, resulting in a processed pyrolysis tar having desirable properties.

[0094] Respecting the properties of TLP and hydroprocessed pyrolysis tar, the density measured at 15°C of the TLP, and particularly the hydroprocessed pyrolysis tar, is typically at

least 0.10 g/cm³ less than the density of the pyrolysis tar feed in conduit 61 of Fig. 1). For example, the density of the TLP and/or the hydroprocessed pyrolysis tar can be at least 0.12, preferably, at least 0.14, 0.15, or 0.17 g/cm³ less than the density of the pyrolysis tar feed. The viscosity measured at 50°C of the TLP (and/or the hydroprocessed pyrolysis tar) is typically < 200 cSt. For example, the viscosity can be < 150 cSt, such as < 100 cSt, or < 75 cSt, or < 50 cSt, or < 40 cSt, or < 30 cSt. Generally, hydroprocessing under Standard Hydroprocessing Conditions results in a significant viscosity improvement over the pyrolysis tar feed. For example, when the viscosity of the raw pyrolysis tar measured at 50°C is $\geq 1.0 \times 10^4$ cSt, e.g., $\geq 1.0 \times 10^5$ cSt, $\geq 1.0 \times 10^6$ cSt, or $\geq 1.0 \times 10^7$ cSt, the viscosity of the TLP and/or hydroprocessed tar measured at 50°C is typically < 200 cSt, e.g., < 150 cSt, preferably, < 100 cSt, < 75 cSt, < 50 cSt, < 40 cSt, or < 30 cSt.

[0095] For a pyrolysis tar feed having an $R_T \leq R_{Ref}$, particularly $2 \cdot R_T \leq R_{Ref}$, more particularly $5 \cdot R_T \leq R_{Ref}$, and even more particularly $10 \cdot R_T \leq R_{Ref}$, the hydroprocessing can be carried out under Standard Hydroprocessing Conditions for a significantly longer duration without significant reactor fouling (e.g., as evidenced by no significant increase in hydroprocessing reactor pressure drop during the desired duration of hydroprocessing, such as a pressure drop of ≤ 140 kPa during a hydroprocessing duration of 10 days, typically ≤ 70 kPa, or ≤ 35 kPa) than is the case under substantially the same hydroprocessing conditions for a pyrolysis tar feed having an $R_T > R_{Ref}$. When $2 \cdot R_T \leq R_{Ref}$, the duration of hydroprocessing without significantly fouling is typically least 10 times longer than would be the case for a pyrolysis tar feed having an $R_T > R_{Ref}$, e.g., ≥ 100 times longer, such as ≥ 1000 times longer. In other words, decreasing R_T to a factor of two below R_{Ref} typically increases the duration of hydroprocessing by at least a factor of ten over the duration achieved at $R_T = R_{Ref}$.

[0096] Processing option available for pyrolysis tar having an $R_T > R_{Ref}$ include hydroprocessing under Mild Hydroprocessing Conditions, which will now be described in more detail. Although hydroprocessing under Mild Hydroprocessing Conditions can be used when the pyrolysis tar has an $R_T \leq R_{Ref}$, the resulting hydroprocessed pyrolysis tar typically has properties that are not as desirable as those achieved when Standard Hydroprocessing Conditions are used.

Mild Hydroprocessing Conditions

[0097] Mild Hydroprocessing Conditions expose the pyrolysis tar feed to less severe conditions than is the case when Standard Hydroprocessing Conditions are used. For example, Compared to Standard Hydroprocessing Conditions, Mild Hydroprocessing Conditions

utilize one or more of a lesser hydroprocessing temperature, a lesser hydroprocessing pressure, a greater hydroprocessor feed WHSV, a greater pyrolysis tar feed WHSV, and a lesser molecular hydrogen consumption rate. Within the parameter ranges (T, P, WHSV, etc.) specified for Mild Hydroprocessing Conditions, particular hydroprocessing conditions for a particular pyrolysis tar feed are typically selected for a desired 566°C+ conversion, typically in the range of from 0.5 wt. % to 5 wt. % substantially continuously for at least ten days.

[0098] For a pyrolysis tar feed having an R_T that is substantially equal to R_{Ref} , the least severe conditions within the Standard Hydroprocessing Conditions which achieve a 566°C+ conversion, of ≥ 20 wt. % substantially continuously for at least ten days are identified as hydroprocessing temperature T_S , hydroprocessing pressure P_S , pyrolysis tar feed space velocity $WHSV_S$, and molecular hydrogen consumption (“ C_S ”). Mild Hydroprocessing Conditions include a temperature hydroprocessing temperature $T_M \geq 150^\circ\text{C}$, e.g., $\geq 200^\circ\text{C}$ but less than T_S (e.g., $T_M \leq T_S - 10^\circ\text{C}$, such as $\leq 400^\circ\text{C}$), a pressure P_M that is ≥ 8 MPa but less than P_S , a pyrolysis tar feed $WHSV_M$ that is $\geq 0.3 \text{ hr}^{-1}$ and greater than $WHSV_S$, and a molecular hydrogen consumption rate (“ C_M ”) that in the range of from 150 standard cubic meters of molecular hydrogen per cubic meter of the pyrolysis tar feed ($S \text{ m}^3/\text{m}^3$) to about 400 $S \text{ m}^3/\text{m}^3$ (845 SCF/B to 2250 SCF/B) but less than C_S .

[0099] Typically, $WHSV_M$ is $> WHSV_S + 0.01$, e.g., $\geq WHSV_S + 0.05 \text{ hr}^{-1}$, such as $\geq WHSV_S + 0.1 \text{ hr}^{-1}$, or $\geq WHSV_S + 0.5 \text{ hr}^{-1}$, or $\geq WHSV_S + 1 \text{ hr}^{-1}$, or $\geq WHSV_S + 10 \text{ hr}^{-1}$, or more. Typically, Mild Hydroprocessing Conditions utilize a lesser temperature (e.g., average bed temperature) than does Standard hydroprocessing, such as $T_M \leq T_S - 25^\circ\text{C}$, such as $T_M \leq T_S - 50^\circ\text{C}$. For example, T_M can be $\leq 440^\circ\text{C}$.

[00100] The higher the R_T measurement is above R_{Ref} , the greater the tendency for the pyrolysis tar to foul, and the greater need to employ the specified blending, the specified Mild Hydroprocessing Conditions, or to closely examine other characteristics of the hydroprocessing which may benefit from modification. Although the foregoing Mild Hydroprocessing Conditions are effective, the invention is not limited thereto. When R_T exceeds R_{Ref} , any hydroprocessing conditions that are effective for reducing fouling may be used. For instance, the speed of the reaction may be decreased by further decreasing the amount of molecular hydrogen provided to the hydroprocessing, or increasing the weight hourly space velocity, or reducing hydroprocessing pressure and/or temperature beyond that specified for Mild Hydroprocessing Conditions.

[00101] For a pyrolysis tar feed having an $R_T > R_{Ref}$, the hydroprocessing can be carried out under Mild Hydroprocessing Conditions for a significantly longer duration without

significant reactor fouling (e.g., as evidenced by no significant increase in hydroprocessing reactor pressure drop) than is the case when hydroprocessing a substantially similar pyrolysis tar feed under Standard Hydroprocessing Conditions. The duration of hydroprocessing without significantly fouling is typically at least 10 times longer than would be the case when
5 hydroprocessing a pyrolysis tar feed having an $R_T > R_{Ref}$ under Standard Hydroprocessing Conditions, e.g., ≥ 100 times longer, such as ≥ 1000 times longer.

Examples

[00102] A lab scale batch thermal treatment (heat soaking) unit is used to heat soak a selected pyrolysis tar at a pressure of 1379 kPa (200 psig) in the presence of N_2 at a plurality
10 of temperatures (200, 250, 300 and 350°C) and residence times (15 minutes, 25 minutes and 45 minutes). BN is determined after each heat soaking test by a method comparable to that disclosed in the Ruzicka article. The tests results, shown in Fig. 2, indicate that in all cases heat soaking decreases pyrolysis tar BN. As shown in the figure, a greater BN decrease is generally achieved with increased heat soak time and increased heat soak temperature.

[00103] Non-heat soaked and heat soaked pyrolysis tars are hydroprocessed over a bed of the specified hydroprocessing catalyst in the presence of the specified utility fluid under Standard Hydroprocessing Conditions including a hydroprocessing temperature $\geq 400^\circ\text{C}$, a
15 pyrolysis tar feed WHSV of 1h^{-1} . Fig. 3 is a graph of pressure drop across the hydroprocessing as a function of hydroprocessing time (in days on stream) for a representative pyrolysis tar. As shown in the figure, an increase in reactor pressure drop (an indication of reactor fouling) occurs within 15 days for the non-heat soaked pyrolysis tar, versus approximately 75 days on stream when the pyrolysis tar is heat soaked at 300°C for a residence time of approximately 30 minutes, and approximately 95 days when the pyrolysis tar is heat soaked at 350°C for a residence time of approximately 30 minutes.
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[00104] Fig. 4 shows that a desirable decrease in in aliphatic olefin content, particularly a decrease in styrenic olefin content, is achieved when the thermal treatment is carried out at a temperature $\geq 350^\circ\text{C}$ for a representative pyrolysis tar. As shown in the figure, the thermal treatment has the desirable feature that it does not significantly change the amount of saturated hydrocarbon and aromatic hydrocarbon in the pyrolysis tar.
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[00105] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.
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[00106] While the illustrative forms disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and

can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the example and descriptions set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

[00107] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

CLAIMS

1. A hydrocarbon conversion process, comprising:

(a) providing a first pyrolysis tar, wherein,

- 5 (i) the first pyrolysis tar contains free radicals and
 (ii) at least 70 wt. % of the first pyrolysis tar has a normal boiling point of at least 290°C;

(b) isolating a sample from the first pyrolysis tar and measuring a reactivity R_T of the sample;

10 (c) comparing R_T to a predetermined reference reactivity R_{Ref} ;

(d) when R_T is greater than a predetermined reference reactivity R_{Ref} ,

 (A) Heating at least a portion of the first pyrolysis tar to achieve a temperature T_{HS} and maintaining the at least a portion of the first
15 pyrolysis tar at a temperature in a range of from T_{HS} to 360°C for a time of time t_{HS} to produce a pyrolysis tar composition, wherein T_{HS} is in the range of from 150°C to 350°C and t_{HS} is ≥ 1 minute,

 (B) isolating a sample from the pyrolysis tar composition and measuring the reactivity R_T of the pyrolysis tar composition sample,
20 and

 (C) repeating step (c); and

(e) when R_T is less than or equal to a predetermined reference reactivity R_{Ref} , hydroprocessing at least a portion of the pyrolysis tar composition to produce a hydroprocessor effluent comprising hydroprocessed pyrolysis tar.

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2. The process of claim 1, wherein (i) R_T and R_{Ref} are determined by a Bromine Number measurement and expressed in BN units, (ii) R_{Ref} is ≤ 20 BN, and (iii) ≥ 90 wt. % of the first pyrolysis tar has a normal boiling point $\geq 290^\circ\text{C}$, (iv) the first pyrolysis tar has a viscosity at 15°C $\geq 1 \times 10^4$ cSt, and (v) the first pyrolysis tar has a
30 density $\geq 1.1 \text{ g/cm}^3$.

3. The process of claim 1, wherein the first pyrolysis tar has an $R_T > 28$ BN, and the

pyrolysis tar composition has an $R_T \leq 18$ BN.

4. The process of claim 1, wherein the hydroprocessed tar has a density measured at 15°C that is at least 0.12 g/cm³ less than the density measured at 15°C of the first pyrolysis tar.

5. The process of claim 1, further comprising carrying out the hydroprocessing in the presence of a utility fluid comprising two-ring and three-ring aromatic hydrocarbon.

6. The process of claim 5, wherein the utility fluid has a $S_{BN} \geq 100$.

7. The process of claim 5, wherein (i) the pyrolysis tar composition and the utility fluid are combined upstream of the hydroprocessing to produce a hydroprocessor feed, and (ii) the hydroprocessor feed comprises the utility fluid in an amount $\leq 10\%$ by weight.

8. The process of claim 1, wherein the hydroprocessing is carried out in at least one hydroprocessing zone operating under Standard Hydroprocessing Conditions in the presence of at least one supported hydroprocessing catalyst which includes at least one metal selected from any of Groups 5 to 10 of the Periodic Table.

9. The process of claim 8, wherein the Standard Hydroprocessing Conditions include a temperature $\geq 200^\circ\text{C}$, a pressure ≥ 8 MPa, a weight hourly space velocity ("WHSV", pyrolysis tar basis) ≥ 0.3 hr⁻¹, and a molecular hydrogen consumption rate in the range of 270 S m³/m³ of molecular hydrogen (based on tar volume) to 534 S m³/m³.

10. The process of claim 1, further comprising:

(f) separating from the hydroprocessor effluent (i) a vapor-phase first stream comprising at least a portion of any unreacted molecular hydrogen, (ii) a liquid-phase second stream comprising at least a portion of the hydroprocessed tar, and (iii) a liquid-phase third stream comprising at least a portion of any unreacted utility fluid;

and

(g) recycling to the hydroprocessing of step (e) at least a portion of the first stream and/or at least a portion of the third stream.

5 11. The process of claim 1, wherein the hydroprocessing of step (d) exhibits a 566°C+ conversion of at least 20 wt. % continuously for at least ten days.

12. The process of claim 1, wherein step (d) further comprises, before step (A) and step (B) therein:

10 (A0) conducting away at least a portion of the first pyrolysis tar or hydroprocessing at least a portion of the first pyrolysis tar under Mild Hydroprocessing Conditions.

13. The process of claim 1, wherein step (d) further comprises, before step (B) 15 therein:

(A1) combining the at least a portion of the first pyrolysis tar with a second pyrolysis tar.