Systems and methods are provided for fixed bed hydroprocessing of deasphalter rock. Instead of attempting to process vacuum resid in a fixed bed processing unit, vacuum resid is deasphalted to form a deasphalted oil and deasphalter residue or rock. The rock can then be hydrotreated in a fixed bed reaction zone, optionally after combining the rock with an aromatic co-feed and/or a hydroprocessing solvent. This can allow for improved conversion of the deasphalter rock and/or improved combined conversion of the deasphalter rock and deasphalted oil.
FIXED BED HYDROPROCESSING OF DEASPHALTER ROCK

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of provisional U.S. Ser. No. 62/196,501, filed Jul. 24, 2015, the entire contents of which are expressly incorporated by reference herein.

FIELD

[0002] Systems and methods are provided for processing of difficult refinery streams, such as rock from a deasphalter unit.

BACKGROUND

[0003] One of the challenges in making effective use of the full range of a crude oil is processing of the vacuum resid portion of a crude oil. Processing of resid feed in a fixed bed process can lead to poor catalyst lifetime and/or processing unit run length if substantial conversion is performed on the 1050°F (+566°C) portion of the feed. The problems with coking of catalyst and reactor run length can be mitigated by use of fluidizing bed or other fluidized fluid technologies. However, such fluidized bed processing methods can present substantial additional challenges relative to fixed bed hydroprocessing.

[0004] U.S. Pat. No. 7,279,090 describes a method for deasphalter a vacuum resid feed and processing the deasphalter rock using an ebulating bed reactor. The examples report 65% to 70% conversion of the deasphalter rock processed in the ebulating bed reactor. The deasphalter oil can be processed either via a fixed bed reactor or an ebulating bed reactor.

SUMMARY

[0005] In an aspect, a method for fixed bed processing of deasphalter rock is provided, comprising: performing solvent deasphalter on a resid feedstock to form a deasphalter rock fraction and a deasphalter oil fraction, the resid feedstock having a T10 distillation point of at least about 650°F (343°C), the deasphalter rock fraction comprising at least about 10 wt % of the resid feedstock; and exposing a feedstock comprising at least a portion of the deasphalter rock fraction to a fixed bed of hydroprocessing catalyst under hydroprocessing conditions effective for conversion of at least 40 wt % of the at least a portion of the deasphalter rock relative to a conversion temperature of 1050°F (566°C) to form a hydroprocessed effluent, the feedstock comprising at least about 10% of the resid feedstock comprising at least about 20 wt % of the co-feed, the feedstock comprising at least about 20 wt % of the deasphalter rock, or at least about 30 wt %, or at least about 40 wt %, or at least about 50 wt %.

BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 shows an example of a reaction system for fixed bed processing a deasphalter rock feed.

[0008] FIG. 2 shows results from processing deasphalter rock with an aromatic solvent.

[0009] FIG. 3 shows results from processing deasphalter rock with an aromatic solvent.

[0010] FIG. 4 shows an example of a reaction system for integrating fixed bed processing a deasphalter rock feed with a fluid catalytic cracking process.

DETAILED DESCRIPTION

[0011] In various aspects, systems and methods are provided for fixed bed hydrotreatment of deasphalter rock. Instead of attempting to process vacuum resid in a fixed bed processing unit, vacuum resid is deasphalted to form a deasphalted oil and deasphalter resid or rock. The rock can then be hydrotreated in a fixed bed reaction zone, optionally after combining the rock with a co-feed and/or a hydrotreating solvent, such as an aromatic petroleum fraction.

[0012] Processing deasphalter rock in the presence of an aromatic petroleum fraction can be in contrast to processing the deasphalter rock in the presence of the deasphalted oil that was separated from the resid to form the rock (i.e., processing the vacuum metal without deasphalter). In contrast to the co-feeds and/or solvents according to the invention, hydrotreatment of a whole vacuum resid (deasphalted oil plus rock) can tend to result in an increase in I_{10}, during processing. As a result, at processing conditions severe enough to convert more than about 35%-50% of the resid, the S/NA of the partially processed resid can become comparable to the I_{10}, leading to asphaltene precipitation and coke formation in a fixed bed environment.

[0013] More generally, it is conventionally understood that conversion of 1050°F (566°C) vacuum resid fractions by hydrotreatment and/or hydrocracking is limited by incompatibility. Under conventional understanding, at somewhere between 30 wt % and 55 wt % conversion of the 1050°F (+566°C) portion, it is conventionally believed that the reaction product becomes incompatible with the feed. For example, as the 1050°F (566°C) feedstock converts to 1050°F (566°C) products, hydrogen transfer, oligomerization, and dealkylation reactions can occur which create molecules that are increasingly difficult to keep in solution. Somewhere between 30 wt % and 55 wt % 1050°F (566°C) conversion, a second liquid hydrocarbon phase separates. This new incompatible phase is believed to be mostly polynuclear aromatics rich in N, S, and metals. The new incompatible phase can also be high in micro carbon residue (MCR). The new incompatible phase can stick to surfaces in the unit where it cokes and then can foul the equipment. Based on the above conventional understanding, it would be expected that hydrotreatment of a feed containing at least about 40 wt % deasphalter rock, or at least about 50 wt %, or at least about 60 wt %, or at least about 40 wt %, would cause incompatibility as the 1050°F (566°C) material is converted to compounds boiling below 1050°F (566°C).
Another conventional alternative can be to perform solvent deasphalting on a vacuum resid to form a deasphalted oil and deasphalter rock. The vacuum resid can then be hydroprocessed, while the deasphalter rock is used as a feed for a coker. Coking of the rock can tend to lead to relatively low liquid product yields, such as around 55 wt % or less. The liquid product yield is correlated with the amount of micro carbon residue of the vacuum resid used to form the deasphalter rock. When the micro carbon residue of the vacuum resid is about 10 wt % or more, the resulting deasphalter rock can tend to have a sufficiently low liquid product yield from coking that this type of process scheme is not favored.

In sharp contrast to this conventional wisdom, it has been discovered that the difficulties in fixed bed hydroprocessing of deasphalter rock (and/or other 1050°F (560°C) + material) can be reduced or minimized by processing the deasphalter rock in an environment with a reduced or minimized content of feed components that are quickly converted into low solubility number fractions. During hydroprocessing of a vacuum resid fraction, at least part of the solvency power for asphaltenes of the vacuum resid fraction is provided by components that may be aromatic in nature, but that can also be rapidly transformed under hydroprocessing conditions to compounds having a lower solvency power. This can result in the solubility number of the vacuum resid fraction being reduced during hydroprocessing at a faster rate than the insolubility number. This problem can be mitigated by performing an initial solvent deasphalting step on a vacuum resid (or alternatively an atmospheric resid) to separate out deasphalted oil and deasphalter rock. In some aspects, the solvent deasphalting can correspond to propane deasphalting, so that propane deasphalter rock is formed. Conventionally, it is understood that the solubility number of deasphalter rock is higher than the solubility number of the corresponding deasphalted oil made during a deasphalting process. As an example, a vacuum resid with a solubility number of about 100 was separated by pentane deasphalting into 75 vol % deasphalted oil with a solubility number of about 80 and 25 vol % deasphalter rock with a solubility number of about 120. It has been discovered that after an initial increase in insolubility number to about 70, the solubility number and insolubility number of the deasphalter rock are reduced at similar rates during hydroprocessing, which can allow for higher levels of conversion of the deasphalter rock while reducing or minimizing coking formation and/or other plugging of a fixed bed reactor.

The fixed bed hydroprocessing of the deasphalter rock can be further facilitated by combining the deasphalter rock with a co-feed that has a solubility number higher than deasphalter rock, such as at least about 110, or at least about 120, and that exhibits similar reduction rates for solubility number and insolubility number during hydroprocessing. An example of such a co-feed is an FCC bottoms fraction. The amount of such co-feed added to the deasphalter rock can be any convenient amount up to about 60 wt %, such as about 1 wt % to 60 wt %, or about 10 wt % to about 50 wt %, or about 15 wt % to about 40 wt %.

Optionally, a portion of the deasphalter rock feed can also correspond to an aromatic solvent that can improve the viscosity or other flow properties of the deasphalter rock. An aromatic solvent can have a final boiling point and/or a T95 distillation point of about 700°F (~371°C) or less and an aromatics content of at least about 50 wt % relative to the weight of the solvent. Such an aromatic solvent can be present in an amount of about 50 wt % or less of the feed for lower boiling solvents, while higher boiling solvents can be limited to about 25 wt % or less. Examples of suitable aromatic solvent can include xylenes and light cycle oils.

FCC bottoms, sometimes referred to as catalytic slurry oil is an example of a suitable co-feed for co-processing with deasphalter rock. Fluid catalytic cracking (FCC) processes commonly be used in refineries to increase the amount of fuels that can be generated from a feedstock. Because FCC processes do not typically involve addition of hydrogen to the reaction environment, FCC processes can be useful for conversion of higher boiling fractions to naphtha and/or distillate boiling range products at a lower cost than hydroprocessing. However, such higher boiling fractions can often contain multi-ring aromatic compounds that are not readily converted, in the absence of additional hydrogen, by the medium pore or large pore molecular sieves typically used in FCC processes. As a result, FCC processes can often generate a bottoms fraction that is highly aromatic in nature. Additionally, the bottoms fraction can also contain catalyst fines generated from the fluidized bed of catalyst during the FCC process. This type of FCC bottoms fraction can also be referred to as a catalytic slurry oil or main column bottoms. Other suitable co-feeds include, but are not limited to, lube extracts, heavy coker gas oils, and vacuum gas oils derived from heavy oils.

Typical FCC bottoms fractions can have a relatively high insolubility number (IN) of about 70 to about 110, which is a measure of the volume percentage of toluene that would be needed to maintain solubility of a given petroleum fraction. According to conventional practices, combining a feed with an IN of greater than about 50 with a virgin crude oil fraction is known to lead to rapid coking under hydroprocessing conditions. However, it has been discovered that such FCC bottoms can be co-processed with deasphalter rock at unexpectedly high levels of conversion in a fixed bed hydroprocessing environment.

In this discussion, reference is made to catalytic slurry oil, FCC bottoms, and main column bottoms. These terms are used interchangeably herein. It is noted that when initially formed, a catalytic slurry oil can include several weight percent of catalyst fines. Such catalyst fines can optionally be removed (such as partially removed to a desired level) by any convenient method, such as filtration. In this discussion, unless otherwise explicitly noted, references to a catalytic slurry oil are defined to include catalytic slurry oil either prior to or after such a process for reducing the content of catalyst fines within the catalytic slurry oil.

In some aspects, reference is made to conversion of a feedstock relative to a conversion temperature T. Conversion relative to a temperature T is defined based on the portion of the feedstock that boils at a temperature greater than the conversion temperature T. The amount of conversion during a process (or optionally across multiple processes) is defined as the weight percentage of the feedstock that is converted from boiling at a temperature above the conversion temperature T to boiling at a temperature below the conversion temperature T. As an illustrative hypothetical example, consider a feedstock that includes 40 wt % of components that boil at 700°F (371°C) or greater. By definition, the remaining 60 wt % of the feedstock boils at less than 700°F (371°C). For such a feedstock, the amount of conversion relative to a conversion temperature of 700°F.
would be based only on the 40 wt % that initially boils at 700° F. (371° C.) or greater. If such a feedstock is exposed to a process with 30% conversion relative to a 700° F. (371° C.) conversion temperature, the resulting product would include 72 wt % of components boiling below 700° F. (371° C.) and 28 wt % of components boiling above 700° F. (371° C.).

Resid Feedstock and Solvent Deasphalting

0022] In various aspects, a resid fraction (or residual fraction) corresponds to a heaviest and/or highest boiling fraction from a temperature based fractionalization process. An atmospheric resid corresponds to a fractionation bottoms from an atmospheric distillation or fractionation. A vacuum resid corresponds to a fractionation bottoms from a vacuum distillation or fractionation. Such resid fractions can have an initial boiling point (such as an initial ASTM D2892 boiling point) of 650° F. (343° C.) or greater. Preferably, a resid fraction can have an 10% distillation point (such as an ASTM D2892 10% distillation point) of at least 650° F. (343° C.), alternatively at least 660° F. (349° C.) or at least 750° F. (399° C.). In some aspects the 10% distillation point can be still greater (corresponding to a vacuum resid), such as at least 900° F. (482° C.), or at least 950° F. (510° C.), or at least 975° F. (524° C.), or at least 1020° F. (549° C.), or at least 1050° F. (566° C.). Such a 10% distillation point can be referred to herein as a “T10 boiling point”. Other fractional weight boiling points, such as T15, T90, or T95 boiling points can be determined in a similar manner.

0023] In addition to resid fractions, reference may be made to one or more types of fractions generated during distillation of a petroleum feedstock. Such fractions may include naphtha fractions, kerosene fractions, diesel fractions, and (vacuum) gas oil fractions. Each of these types of fractions can be defined based on a boiling range, such as a boiling range that includes at least 90 wt % of the fraction (T90 boiling point), and preferably at least 95 wt % of the fraction (T95 boiling point). For example, for many types of naphtha fractions, at least 90 wt % of the fraction, and preferably at least 95 wt %, can have a boiling point in the range of 85° F. (29° C.) to 350° F. (177° C.). For some heavier naphtha fractions, at least 90 wt % of the fraction, and preferably at least 95 wt %, can have a boiling point in the range of 85° F. (29° C.) to 400° F. (204° C.). For a kerosene fraction, at least 90 wt % of the fraction, and preferably at least 95 wt %, can have a boiling point in the range of 500° F. (260° C.) to 600° F. (316° C.). Alternatively, for a kerosene fraction targeted for some uses, such as jet fuel production, at least 90 wt % of the fraction, and preferably at least 95 wt %, can have a boiling point in the range of 500° F. (260° C.) to 550° F. (288° C.). For a diesel fraction, at least 90 wt % of the fraction, and preferably at least 95 wt %, can have a boiling point in the range of 400° F. (204° C.) to 750° F. (399° C.). Although feedstocks in the light to middle distillate boiling range can typically be assessed according to ASTM D2887, if a feedstock or other sample contains components not suitable for characterization using D2887, other standard methods, such as ASTM D1160 and/or ASTM D2892, may be used instead for such component.

0024] Typical gas oil fractions can include, for example, fractions with an initial boiling point of at least about 650° F. (343° C.), or at least about 700° F. (371° C.), or at least about 750° F. (399° C.). Alternatively, a gas oil fraction may be characterized using a T5 boiling point, such as a fraction with a T5 boiling point of at least about 650° F. (343° C.), or at least about 700° F. (371° C.), or at least about 750° F. (399° C.). In some aspects, the final boiling point of a gas oil fraction can be about 1100° F. (605° C.) or less, such as about 1100° F. (593° C.) or less, or about 1050° F. (566° C.) or less. Alternatively, a gas oil fraction may be characterized using a T95 boiling point, such as a fraction with a T95 boiling point of at least about 1100° F. (605° C.) or less, or about 1100° F. (593° C.) or less, or about 1050° F. (566° C.) or less. In still other aspects, a gas oil fraction can correspond to a lower boiling gas oil fraction, with a T95 boiling point or final boiling point of about 1000° F. (538° C.) or less, such as about 950° F. (510° C.) or less. An example of a suitable type of gas oil fraction is a wide cut vacuum gas oil (VGO), with a T5 boiling point of at least about 700° F. (371° C.) and a T95 boiling point of about 1100° F. (593° C.) or less, preferably a T95 boiling point of about 1000° F. (538° C.) or less.

0025] After forming a resid fraction, such as a vacuum resid fraction, a solvent deasphalting process can be used to separate deasphalted oil from deasphalted rock. Solvent deasphalting is a solvent extraction process. Typical solvents include alkanes or other hydrocarbons containing about 3 to about 6 carbons per molecule. Examples of suitable solvents include propane, n-butane, isobutane, and n-pentane. In some aspects, propane deasphalting can be used, which can increase the amount of deasphalted rock that is generated. Alternatively, other types of solvents may also be suitable, such as supercritical fluids. During solvent deasphalting, a feed portion is mixed with the solvent. Portions of the feed that are soluble in the solvent are then extracted, leaving behind a residue with little or no solubility in the solvent. Typical solvent deasphalting conditions include mixing a feedstock fraction with a solvent in a weight ratio of from about 1:2 to about 1:10, such as about 1:8 or less. Typical solvent deasphalting temperatures range from about 40° C. to about 150° C. The pressure during solvent deasphalting can be from about 50 psig (≈345 kPag) to about 500 psig (≈3.4 MPag).

0026] The portion of the deasphalted feedstock that is extracted with the solvent is often referred to as deasphalted oil. The yield of deasphalted oil from a solvent deasphalting process varies depending on a variety of factors, including the nature of the feedstock, the type of solvent, and the solvent extraction conditions. A lighter molecular weight solvent such as propane will result in a lower yield of deasphalted oil as compared to n-pentane, as fewer components of a bottoms fraction will be soluble in the shorter chain alkanes. However, the deasphalted oil resulting from propane deasphalting is typically of higher quality, resulting in expanded options for use of the deasphalted oil. Under typical deasphalting conditions, increasing the temperature will also usually reduce the yield while increasing the quality of the resulting deasphalted oil. In various embodiments, the yield of deasphalted oil from solvent deasphalting can be about 85 wt % or less of the feed to the deasphalting process, or about 75 wt % or less. The deasphalted oil resulting from the solvent deasphalting procedure can then be optionally exposed to a solvent extraction process. After a deasphalting process, the yield of deasphalted rock can be at least about 15 wt % of the feed to the deasphalting process, or at least about 20 wt %, or at least about 25 wt %, or at least about 30 wt %, or at least about 35 wt %, or at least
about 40 wt %, and/or about 75 wt % or less, or about 65 wt % or less, or about 50 wt % or less, or about 40 wt % or less, or about 30 wt % or less, or about 25 wt % or less. Each of the above lower bounds for the amount of deasphalted rock yield is explicitly contemplated in conjunction with each of the above upper bounds.

[0027] In some aspects, the deasphalted oil can be exposed to further processing to form Group I lubricant base stocks. For example, two types of additional solvent processing can be performed. The first type of solvent processing is solvent extraction to reduce the aromatics content and/or the amount of polar molecules. The solvent extraction process selectively dissolves aromatic components to form an aromatics-rich extract phase (sometimes referred to as a lubes extract) while leaving the more paraffinic components in an aromatics-poor raffinate phase. Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrroldone. By controlling the solvent to oil ratio, extraction temperature and method of contacting distillate to be extracted with solvent, one can control the degree of separation between the extract and raffinate phases. Any convenient type of liquid-liquid extractor can be used, such as a counter-current liquid-liquid extractor. Depending on the initial concentration of aromatics in the deasphalted bottoms, the raffinate phase can have an aromatics content of about 10 wt % to about 50 wt %.

[0028] In some aspects, the raffinate from the solvent extraction can be under-extracted. In such aspects, the extraction is carried out under conditions such that the raffinate yield is maximized while still removing most of the lowest quality molecules from the feed. Raffinate yield may be maximized by controlling extraction conditions, for example, by lowering the solvent to oil treat ratio and/or decreasing the extraction temperature. The raffinate from the solvent extraction unit can then be solvent dewaxed under solvent dewaxing conditions to remove hard waxes from the raffinate.

[0029] Solvent dewaxing typically involves mixing the raffinate feed from the solvent extraction unit with chilled dewaxing solvent to form an oil-solvent solution. Precipitated wax is thereafter separated by, for example, filtration. The temperature and solvent are selected so that the oil is dissolved by the chilled solvent while the wax is precipitated.

[0030] An example of a suitable solvent dewaxing process involves the use of a cooling tower where solvent is pre-chilled and added incrementally at several points along the height of the cooling tower. The oil-solvent mixture is agitated during the chilling step to permit substantially instantaneous mixing of the prechilled solvent with the oil. The prechilled solvent is added incrementally along the length of the cooling tower so as to maintain an average chilling rate at or below 10° F. per minute, usually between about 1° F. to about 5° F. per minute. The final temperature of the oil-solvent/precipitated wax mixture in the cooling tower will usually be between 0 and 50° F. (−18 to 10° C.). The mixture may then be sent to a scraped surface chiller to separate precipitated wax from the mixture.

[0031] Representative dewaxing solvents are aliphatic ketones having 3–6 carbon atoms such as methyl ethyl ketone and methyl isobutyl ketone, low molecular weight hydrocarbons such as propane and butane, and mixtures thereof. The solvents may be mixed with other solvents such as benzene, toluene or xylene.

[0032] In general, the amount of solvent added will be sufficient to provide a liquid/solid weight ratio between the range of 5/1 and 20/1 at the dewaxing temperature and a solvent/oil volume ratio between 1.5/1 to 5/1. The solvent dewaxed oil is typically dewaxed to an intermediate pour point, preferably less than about +10° C., such as less than about 5° C. or less than about 0° C. The resulting solvent dewaxed oil is suitable for use in forming one or more types of Group I base oils. The aromatics content will typically be greater than 10 wt % in the solvent dewaxed oil. Additionally, the sulfur content of the solvent dewaxed oil will typically be greater than 300 wppm.

Additional Feedstocks and Solvents—Aromatic Feeds, Light Cycle Oil, Catalytic Slurry Oil

[0033] In various aspects, the amount of deasphalted rock in a feed for fixed bed hydroprocessing can be at least about 10 wt % of the feed, or at least about 20 wt %, or at least about 30 wt %, or at least about 40 wt %, or at least about 50 wt %, or at least about 60 wt %. Deasphalted rock can tend to be a high viscosity fraction, and may even be a solid or semi-solid fraction at ambient temperature. In order to facilitate introducing the deasphalted rock into a reactor for fixed bed hydroprocessing, in some aspects the deasphalted rock can be co-processed with an additional aromatic co-feed and/or aromatic solvent in order to modify the flow properties of the deasphalted rock feed. One option can be to add an additional aromatic feed that has similar behavior during hydroprocessing to deasphalted rock. An example of a suitable aromatic co-feed can be FCC bottoms, also referred to as catalytic slurry oil. Other examples of suitable aromatic co-feeds can include, but are not limited to, heavy coker gas oils, lube extracts, and vacuum gas oils derived from heavy oils.

[0034] A catalytic slurry oil can correspond to a high boiling fraction, such as a bottoms fraction, from an FCC process. A variety of properties of a catalytic slurry oil can be characterized to specify the nature of a catalytic slurry oil feed.

[0035] One aspect that can be characterized is a boiling range of the catalytic slurry oil. Typically the cut point for forming a catalytic slurry oil can be at least about 650° F. (343° C.). As a result, a catalytic slurry oil can have a T5 distillation (boiling) point or a T10 distillation point of at least about 650° F. (343° C.), as measured according to ASTM D2887. In some aspects the D2887 10% distillation point can be greater, such as at least about 675° F. (357° C.), or at least about 700° F. (371° C.). In other aspects, a broader boiling range portion of FCC products can be used as a feed, where the broader boiling range portion includes a 650° F. fraction that corresponds to a catalytic slurry oil. It is noted that the catalytic slurry oil (650° F. to 343° C.) fraction of the feed does not necessarily have to represent a “bottoms” fraction from an FCC process, so long as the catalytic slurry oil portion has one or more of the other feed characteristics described herein.

[0036] In addition to initial boiling points, T5 distillation point, and/or T10 distillation points, other distillation points may also be useful in characterizing a feedstock. For example, a feedstock can be characterized based on the portion of the feedstock that boils above 1050° F. (566° C.). In some aspects, a feedstock (or alternatively a 650° F.+/
Density, or weight per volume, of the catalytic slurry oil can also be characterized. In various aspects, the density of the catalytic slurry oil (or alternatively a 650°F E+ portion of a feedstock) can be at least about 1.06 g/cc, or at least about 1.08 g/cc, or at least about 1.10 g/cc. The density of the catalytic slurry oil can provide an indication of the amount of heavy aromatic cores that are present within the catalytic slurry oil. A lower density catalytic slurry oil feed can in some instances correspond to a feed that may have a greater expectation of being suitable for hydrotreatment without substantial and/or rapid coke formation.

Contaminants such as nitrogen and sulfur are typically found in catalytic slurry oils, often in organically-bound form. Nitrogen content can range from about 50 wppm to about 5000 wppm elemental nitrogen, or about 100 wppm to about 2000 wppm elemental nitrogen, or about 250 wppm to about 1000 wppm, based on total weight of the catalytic slurry oil. The nitrogen containing compounds can be present as basic or non-basic nitrogen species. Examples of nitrogen species include quinolones, substituted quinolones, carbazoles and substituted carbazoles.

The sulfur content of a catalytic slurry oil feed can be at least about 500 wppm elemental sulfur, based on total weight of the catalytic slurry oil. Generally, the sulfur content of a catalytic slurry oil can range from about 500 wppm to about 100,000 wppm elemental sulfur, or from about 1000 wppm to about 50,000 wppm, or from about 1000 wppm to about 30,000 wppm, based on total weight of the heavy component. Sulfur can usually be present as organically bound sulfur. Examples of such sulfur compounds include the class of heterocyclic sulfur compounds such as thiophenes, tetrahydrothiophenes, benzothiophenes and their higher homologs and analogs. Other organically bound sulfur compounds include aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides.

Catalytic slurry oils can also include n-heptane insoluble (NHI) or asphaltene. In some aspects, the catalytic slurry oil feed (or alternatively a 650°F E+ portion of a feed) can contain at least about 3 wt % of n-heptane asphaltene, or at least about 5 wt %, and/or up to about 10 wt %. Another option for characterizing the heavy components of a catalytic slurry oil can be based on the amount of micro carbon residue (MCR) in the feed. In various aspects, the amount of MCR in the catalytic slurry oil feed (or alternatively a 650°F E+ portion of a feed) can be at least about 5 wt %, or at least about 8 wt %, or at least about 10 wt %, and/or up to about 16 wt %.

Based on the content of NHI and/or MCR in a catalytic slurry oil feed, the insolubility number (IN) for such a feed can be at least about 60, or at least about 70, or at least about 80, or at least about 90. Additionally or alternately, the IN for such a feed can be about 140 or less, or about 120 or less, or about 110 or less, or about 100 or less, or about 90 or less, or about 80 or less. It is noted that each lower bound noted above for IN is explicitly contemplated in conjunction with each upper bound noted above for IN. Additionally or alternately, each lower bound noted above for IN is explicitly contemplated in conjunction with each lower and/or upper bound noted above for NHI and/or MCR.

With regard to heavy coker gas oils, suitable heavy coker gas oils can have an initial boiling point or TS distillation point of at least about 600°F (−316°C), and/or a T10 distillation point of at least about 650°F (−343°C), and a T90 distillation point of at least about 1050°F (−566°C), or less, and/or a T95 distillation point or final boiling point of about 1150°F (−621°C) or less, or about 1100°F (−593°C) or less. Similar to main column bottoms, heavy coker gas oils can have a sufficiently high solubility number and/or a sufficiently low rate of solubility number reduction to allow for co-processing of heavy coker gas oils with desaltsphaler rock.

Lube extracts refer to aromatic extract fractions that can be formed during solvent processing of a feedstock to form (Group 1) lubricant base stocks. Similar to main column bottoms, lube extracts fractions can have a sufficiently high solubility number and/or a sufficiently low rate of solubility number reduction to allow for co-processing of lube extracts with desaltsphaler rock.

Still another potential co-feed can be a vacuum gas oil derived from a heavy oil. Heavy oils can have an initial boiling point (measured by, e.g., ASTM D2887) of 650°F (343°C) or greater and/or a 10% distillation point at least 650°F (343°C), or at least 660°F (349°C), or at least 750°F (399°C). In some aspects the 10% distillation point can be still greater, such as at least 950°F (510°C), or at least 1020°F (549°C), or at least 1050°F (566°C). In addition to initial boiling points and/or 10% distillation points, other distillation points may also be useful in characterizing a heavy oil. For example, a feedstock can be characterized based on the portion of the feedstock that boils above 1050°F (566°C). In some aspects, a feedstock can have a 70% distillation point of 1050°F (566°C) or greater, or a 60% distillation point of 1050°F (566°C) or greater, or a 50% distillation point of 1050°F (566°C) or greater, or a 40% distillation point of 1050°F or greater. A vacuum gas oil derived from such a heavy oil can have a typical boiling range for a vacuum gas oil, such as a T5 distillation point of at least about 650°F (−343°C), or at least about 700°F (−371°C), and a T95 distillation point of about 1100°F (−593°C) or less, or about 1050°F (−566°C) or less, or about 1000°F (−538°C) or less. Similar to main column bottoms, a vacuum gas oil derived from such a heavy oil feed can have a sufficiently high solubility number and/or a sufficiently low rate of solubility number reduction to allow for co-processing of the vacuum gas oil with desaltsphaler rock.

In some aspects, an aromatic solvent can also be added to the desaltsphaler rock feed. An aromatic solvent can assist with the flow properties of the desaltsphaler rock feed. The aromatic solvent can have a final boiling point of about 400°C or less, or about 375°C or less, or about 350°C or less. In order to reduce or minimize incompatibility issues, the amount of the aromatic solvent can be about 50 wt % or less of the feed, or about 40 wt % or less, or about 30 wt % or less, or about 20 wt % or less, or about 10 wt % or less. The amount of aromatic solvent can also be dependent on the boiling range of the solvent. For a solvent having a final boiling point or a TS5 boiling point of at least about 300°C, the amount of the aromatic solvent can be about 40 wt % or less, or about 30 wt % or less, or about 20 wt % or less, or about 10 wt % or less. For a solvent having a final boiling point or a TS5 boiling point of at least about 350°C, the amount of the aromatic solvent
can be about 30 wt % or less, or about 25 wt % or less, or about 20 wt % or less, or about 10 wt % or less. For a solvent having a final boiling point or a T95 boiling point of at least about 400 °C, the amount of aromatic solvent can be about 25 wt % or less, or about 15 wt % or less, or about 10 wt % or less.

[0046] Additionally or alternately, at least a minimum amount of a co-feed, an aromatic solvent, or a combination thereof can be introduced into the fluid bed hydropyroprocessing environment with the desphalter rock feed. For example, the at least a minimum amount of co-feed, aromatic solvent, or a combination thereof can be combined with the desphalter rock to facilitate flow of the desphalter rock into and/or through the fixed bed environment. In such aspects, the desphalter rock can be exposed to the fixed bed of hydropyroprocessing catalyst in the presence of at least about 10 wt % of aromatic co-feed, aromatic solvent, or a combination thereof, or at least about 15 wt %, or at least about 20 wt %, or at least about 25 wt %.

[0047] One option for an aromatic solvent can be a solvent corresponding to one or a few chemical compounds. Examples of individual compounds that can be included in an aromatic solvent include, but are not limited to, xylene, alkylated benzenes, and/or other aromatic compounds with a boiling point between about 120 °C to about 400 °C, or about 120 °C to about 350 °C, or about 120 °C to about 300 °C, or about 120 °C to about 250 °C, or about 150 °C to about 400 °C, or about 150 °C to about 350 °C, or about 150 °C to about 300 °C, or about 150 °C to about 250 °C, or about 250 °C to about 350 °C, or about 250 °C to about 300 °C, or about 250 °C to about 250 °C.

[0048] Another option for an aromatic solvent can be to use one or more refinery streams. The one or more refinery streams can have a combined aromatic content of at least about 50 wt % relative to the weight of the aromatic solvent, or at least about 60 wt %. Examples of suitable refinery streams for use as an aromatic solvent include, but are not limited to, light cycle oils, coker gas oils, and/or other refinery streams having a boiling range between about 120 °C to about 500 °C, or about 120 °C to about 450 °C, or about 120 °C to about 400 °C, or about 120 °C to about 350 °C, or about 120 °C to about 300 °C, or about 120 °C to about 250 °C, or about 150 °C to about 500 °C, or about 150 °C to about 450 °C, or about 150 °C to about 400 °C, or about 150 °C to about 350 °C, or about 150 °C to about 300 °C, or about 150 °C to about 250 °C, or about 200 °C to about 550 °C, or about 200 °C to about 500 °C, or about 200 °C to about 450 °C, or about 200 °C to about 400 °C, or about 200 °C to about 350 °C, or about 200 °C to about 300 °C, or about 250 °C to about 550 °C, or about 250 °C to about 500 °C, or about 250 °C to about 450 °C, or about 250 °C to about 400 °C, or about 250 °C to about 350 °C. It is noted that the above boiling ranges can correspond to an initial boiling point or a T5 boiling point to a final boiling point or a T95 boiling point.

Fixed Bed Hydrotreatment

[0049] Conventionally, feeds having an IN of greater than about 50 have been viewed as unsuitable for fixed bed hydropyroprocessing. This conventional view is due to the belief that feeds with an IN of greater than about 50 are likely to cause substantial formation of coke within a reactor, leading to rapid plugging of a fixed reactor bed. Instead of using a fixed bed reactor, feeds with a high IN value are conventionally processed using other types of reactors that can allow for regeneration of catalyst during processing, such as a fluidized bed reactor. Alternatively, if a fixed bed catalyst is used for conventional processing of a high IN feed, the conditions are conventionally selected to achieve a low amount of conversion in the feed relative to a conversion temperature of 1050 °F (566 °C), such as less than about 30% to about 50% conversion. Performing a limited amount of conversion on a high IN feed is conventionally believed to be required to avoid rapid precipitation and/or coke formation within a fixed bed reactor.

[0050] In various aspects, a feed composed of a substantial portion of desphalter rock can be hydrotreated under effective hydrotreating conditions to form a hydrotreated effluent. The effective hydrotreating conditions can allow for conversion of at least about 55 wt % of the desphalter rock relative to 1050 °F (566 °C), or at least about 60 wt %, or at least about 65 wt %, or at least about 70 wt %. It is noted that when desphalter rock is formed by a desphalting process, a desphalted oil fraction is also formed. This desphalted oil fraction can be substantially completely converted in a separate process, such as a fixed bed hydrotreatment process. Based on the combined conversion of the desphalted oil and the desphalter rock, at least about 80 wt % of the 1050 °F (566 °C) portion of a vacuum resid can be achieved, or at least about 85 wt %.

[0051] Hydrotreating (such as hydrotreating) is carried out in the presence of hydrogen. A hydrogen stream can be fed or injected into a vessel or reaction zone or hydropyroprocessing zone in which the hydrotreating catalyst is located. Hydrogen, which is contained in a hydrogen “treat gas,” is provided to the reaction zone. Treat gas, as referred to herein, can be either pure hydrogen or a hydrogen-containing gas, which is a gas stream containing hydrogen in an amount that is sufficient for the intended reaction(s), optionally including one or more other gasses (e.g., nitrogen and light hydrocarbons such as methane), and which will not adversely interfere with or affect either the reactions or the products. Impurities, such as H₂S and NH₃ are undesirable and would typically be removed from the treat gas before it is conducted to the reactor. In aspects where the treat gas stream is different from a stream that substantially consists of hydrogen (i.e., at least about 99 vol % hydrogen), the treat gas stream introduced into a reaction stage can contain at least about 50 vol %, or at least about 75 vol % hydrogen, or at least about 90 vol % hydrogen.

[0052] In some aspects, a combination of catalysts can be used for hydropyroprocessing of a heavy oil feed. For example, a heavy oil feed can be contacted first by a demetallation catalyst, such as a catalyst including NiMo or CoMo on a support with a median pore diameter of 200 Å or greater. A demetallation catalyst represents a lower activity catalyst that is effective for removing at least a portion of the metals content of a feed. This allows a less expensive catalyst to be used to remove a portion of the metals, thus extending the lifetime of any subsequent higher activity catalysts. The demetallized effluent from the demetallation process can then be contacted with a conventional hydrotreating catalyst.

[0053] Contacting conditions in the contacting or hydropyroprocessing zone can include, but are not limited to, temperature, pressure, hydrogen flow, hydrocarbon feed flow, or combinations thereof. Contacting conditions in some embodiments are controlled to yield a product with specific properties.

[0054] Hydrotreating is carried out in the presence of hydrogen. A hydrogen stream is, therefore, fed or injected.
into a vessel or reaction zone or hydroprocessing zone in which the hydroprocessing catalyst is located. Hydrogen, which is contained in a hydrogen “treat gas,” is provided to the reaction zone. Treat gas, as referred to herein, can be either pure hydrogen or a hydrogen-containing gas, which is a gas stream containing hydrogen in an amount that is sufficient for the intended reaction(s), optionally including one or more other gases (e.g., nitrogen and light hydrocarbons such as methane), and which will not adversely interfere with or affect either the reactions or the products. Impurities, such as H₂S and NH₃, are undesirable and would typically be removed from the treat gas before it is conducted to the reactor. The treat gas stream introduced into a reaction stage will preferably contain at least about 50 vol. % and more preferably at least about 75 vol. % hydrogen.

Based on the reaction conditions described above, in various aspects of the invention, a portion of the reactions taking place in the hydroprocessing reaction environment can correspond to thermal cracking reactions. In addition to the reactions expected during hydroprocessing of a feed in the presence of hydrogen and a hydroprocessing catalyst, thermal cracking reactions can also occur at temperatures of 360° C. and greater. In the hydroprocessing reaction environment, the presence of hydrogen and catalyst can reduce the likelihood of coke formation based on radicals formed during thermal cracking.

In an embodiment of the invention, contacting the input feed in the hydroconversion reactor with the hydroprocessing catalyst in the presence of hydrogen to produce a hydroprocessed product is carried out in a single contacting zone. In another aspect, contacting is carried out in two or more contacting zones.

In an aspect, the hydrotreating step may comprise at least one hydrotreating reactor, and optionally may comprise two or more hydrotreating reactors arranged in series flow. A vapor separation drum can optionally be included after each hydrotreating reactor to remove vapor phase products from the reactor effluent(s). The vapor phase products can include hydrogen, H₂S, NH₃, and hydrocarbons containing four (4) or less carbon atoms (i.e., “C4-hydrocarbons”). The effective hydrotreating conditions can be suitable for removal of at least about 70 wt %, or at least about 80 wt %, or at least about 90 wt % of the sulfur content in the feedstream from the resulting liquid products. Additionally or alternatively, at least about 50 wt %, or at least about 75 wt % of the nitrogen content in the feedstream can be removed from the resulting liquid products. In some aspects, the final liquid product from the hydrotreating unit can contain less than about 10000 ppmw sulfur, or less than about 5000 ppmw sulfur, or less than about 1000 ppmw sulfur.

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Examples of suitable metals include Ni, W, Mo, Co and mixtures thereof, for example CoMo, NiMoW, NixMo, or NiW. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. The amount of metals for supported hydroprocessing catalysts, either individually or in mixtures, can range from 0.5 to 35 wt %, based on the weight of the catalyst. Additionally or alternatively, for mixtures of Group VIA and Group VIII metals, the Group VIII metals are present in amounts of from 0.5 to 5 wt % based on catalyst, and the Group VIA metals are present in amounts of from 5 to 30 wt % based on the catalyst. A mixture of metals may also be present as a bulk metal catalyst wherein the amount of metal is 30 wt % or greater, based on catalyst weight.

Suitable metal oxide supports for the hydroprocessing catalysts include oxides such as silica, alumina, silica-alumina, titania, or zirconia. Examples of aluminas suitable for use as a support can include porous aluminas such as gamma or eta. In some cases, when a porous metal oxide support is utilized, the catalyst can have an average pore size.
(as measured by nitrogen adsorption) of about 30 Å to about 1000 Å, or about 50 Å to about 500 Å, or about 60 Å to about 300 Å. Porosity can be determined, for example, according to ASTM Method D4284-07 Mercury Porosimetry. Additionally or alternately, the catalyst can have a surface area (as measured by the BET method) of about 100 to 350 m²/g, or about 150 to 250 m²/g. In some aspects, a supported hydrotreating catalyst can have the form of shaped extrudates. The extrudate diameters can range from ½₂⁸ to ⅛₈₁₈ inch, from ⅛₈₁₈ to ⅛₈₂₆ inch, or from ⅛₂₆ to ¼₈₅₄ inch. The extrudates can be cylindrical or shaped. Non-limiting examples of extrudate shapes include trilobes and quadrilobes.

[0065] In various aspects, the deasphalted oil formed after deasphalteration can also be hydroprocessed in any convenient manner, such as by the fixed bed hydroprocessing. One option can be to separate the process the deasphalted oil under conditions similar to those described above. In other aspects, suitable conditions for processing a deasphalted oil can be similar to conditions for hydrotreatment of a vacuum gas oil boiling range feed. For example, hydrotreating conditions can include temperatures of 200°C to 430°C, or 315°C to 420°C; pressures of 250 psig (1.8 MPag) to 5000 psig (34.6 MPag) or 300 psig (2.1 MPag) to 5000 psig (20.8 MPag); liquid hourly space velocities (LHSV) of 0.1 hr⁻¹ to 10 hr⁻¹; and hydrogen treat rates of 200 scf/B (35.6 m³/m³) to 10,000 scf/B (1780 m³/m³), or 500 (89 m³/m³) to 5,000 scf/B (890 m³/m³).

Product Properties—Hydrotreated Effluent

[0066] Processing a resid feed in the manner described above, so that a deasphalted oil portion and a deasphalter rock portion are separately hydroprocessed using fixed bed hydrotreatment, can allow for improved yield relative to fixed bed hydroprocessing of the resid feed while providing for a commercial viable run length for the reaction system. In various aspects, the conversion of the deasphalter rock relative to a conversion temperature of 1050°F (566°C) can be at least about 40 wt %, or at least about 50 wt %, or at least about 55 wt %, or at least about 60 wt %, or at least about 65 wt %, or at least about 70 wt %, or at least about 75 wt %. Additionally or alternately, the high degree of conversion of the deasphalter rock can allow for high levels of conversion of the combined deasphalted oil (DAO) and deasphalter rock. For example, separation of a resid into 60 wt % DAO and 40 wt % rock, followed by 95 wt % conversion of the DAO and 40 wt % conversion of the rock results in an overall resid 1050°F (566°C) conversion of 73%. In various aspects, the conversion of the combined deasphalted oil and deasphalted rock relative to 1050°F (566°C) can be at least about 60 wt %, or at least about 65 wt %, or at least about 70 wt %, or at least about 75 wt %, or at least about 80 wt %.

[0067] Another method for characterizing the hydrotreatment of the deasphalter rock can be based on the asphaltene content of the hydrotreated product. In some aspects, the deasphalter rock can have an asphaltene content (defined as n-heptane insolubles) of about 10 wt % to about 50 wt %, or at least about 15 wt %, or at least about 20 wt %, and/or about 40 wt % or less, or about 50 wt % or less. After hydrotreating, the amount of asphaltenes in the hydrotreated effluent can be about 50 wt % or less of the amount of asphaltenes in the feed containing the deasphalter rock, or about 40 wt % or less, or about 30 wt % or less, or about 20 wt % or less, or about 10 wt % or less.

[0068] After hydrotreatment (or other hydroprocessing), the hydrotreated (or hydrosulfided) effluent from the deasphalter rock and/or the hydrotreated effluent from the deasphalted oil can be processed in any further convenient manner. For example, the hydrotreated effluent from the deasphalter rock and/or the hydrotreated effluent from the deasphalted oil can be hydrotreated, processed in a fluid catalytic cracker, or treated in another conventional refinery process for processing of gas oil boiling range feeds.

[0069] After hydrotreatment of the deasphalter rock, the liquid (C₆₊) portion of the hydrotreated effluent can have a volume that is at least about 95% of the volume of the catalytic slurry oil feed, or at least about 100% of the volume of the feed, or at least about 105%, or at least about 110%, such as up to about 150% of the volume. It is noted that C₂ and C₄ hydrocarbons can be used, for example, to form liquefied propane or butane gas as a potential liquid product. Therefore, the C₆₊ portion of the effluent is counted as the “liquid” portion of the effluent product, even though a portion of the compounds in the liquid portion of the hydrotreated effluent may exit the hydrotreatment reactor (or stage) as a gas phase at the exit temperature and pressure conditions for the reactor.

[0070] Additionally or alternately, after hydrotreatment of the deasphalter rock, the sulfur content of the liquid (C₆₊) portion of the hydrotreated effluent can be about 2000 ppm or less, or about 1000 ppm or less, or about 5000 ppm or less, or about 3000 ppm or less, or about 1000 ppm or less, such as at least about 1 ppm, or at least about 100 ppm. Additionally or alternately, the sulfur content of the hydrotreated effluent can be reduced by at least about 50% relative to the sulfur content of the deasphalter rock, or at least about 60%, or at least about 70%, or at least about 80%.

[0071] Additionally or alternately, the micro carbon residue of the hydrotreated effluent can be reduced by at least about 50% relative to the micro carbon residue of the deasphalter rock, or at least about 60%, or at least about 70%, or at least about 80%.

[0072] Additionally or alternately, the hydrogen content of the liquid (C₆₊) portion of the hydrotreated effluent from processing of the deasphalter rock can be at least about 9.5 wt %, or at least about 10.0 wt %, or at least about 10.5 wt %, or at least about 11.0 wt %, or at least about 11.5 wt %.

ADDITIONAL EMBODIMENTS

Embodiment 1

[0073] A method for fixed bed processing of deasphalter rock, comprising: performing solvent deasphalting on a resid feedstock to form a deasphalter rock fraction and a deasphalted oil fraction, the resid feedstock having a T10 distillation point of at least about 650°F (~343°C), the deasphalter rock fraction comprising at least about 10 wt % of the resid feedstock; and exposing a feedstock comprising at least a portion of the deasphalter rock fraction to a fixed bed of hydrotreating catalyst under hydrotreating conditions effective for conversion of at least 40 wt % of the at least a portion of the deasphalter rock relative to a conversion temperature of 1050°F (566°C) to form a hydrotreated effluent; the feedstock comprising at least about 10 wt % of the at least a portion of the deasphalter rock, or at least
about 20 wt %, or at least about 30 wt %, or at least about 40 wt %, or at least about 50 wt %.

Embodiment 2

[0074] A method for fixed bed processing of deasphalter rock, comprising: exposing a feedstock comprising deasphalter rock and a co-feed comprising a catalytic slurry oil, a liquescent extract, a heavy coker gas oil, a vacuum gas oil derived from a heavy oil, or a combination thereof, to a fixed bed of hydrotreating catalyst under hydrotreating conditions effective for conversion of at least 40 wt % of the deasphalter rock relative to a conversion temperature of 1050° F. (566° C.) to form a hydrotreated effluent, the feedstock comprising at least about 20 wt % of the co-feed, the feedstock comprising at least about 10 wt % of the deasphalter rock, or at least about 20 wt %, or at least about 30 wt %, or at least about 40 wt %, or at least about 50 wt %.

Embodiment 3

[0075] The method of Embodiment 2, further comprising performing solvent deasphalting on a resid feedstock to form at least the deasphalter rock and a deasphalted oil fraction, the resid feedstock having a T10 distillation point at least about 650° F. (~343° C.), the deasphalter rock comprising at least about 10 wt % of the resid feedstock.

Embodiment 4

[0076] The method of any of Embodiments 2 to 3, wherein the feedstock comprises at least about 20 wt % of the catalytic slurry oil, or at least about 30 wt %, or at least about 40 wt %, or at least about 50 wt %.

Embodiment 5

[0077] The method any of Embodiments 2 to 4, wherein the feedstock comprises at least about 30 wt % of the co-feed, or at least about 40 wt %, or at least about 50 wt %.

Embodiment 6

[0078] The method of any of the above embodiments, wherein the feedstock further comprises an aromatic solvent, the aromatic comprising at least 50 wt % of aromatic compounds relative to a weight of the aromatic solvent, the aromatic solvent having a boiling range from about 100° C. to about 500° C., the aromatic solvent optionally comprising a light cycle oil.

Embodiment 7

[0079] The method of Embodiment 6, wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 300° C. or less, or wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 350° C. or less and the feedstock comprises about 40 wt % or less of the aromatic solvent; or wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 400° C. or less and the feedstock comprises about 50 wt % or less of the aromatic solvent.

Embodiment 8

[0080] The method of any of the above embodiments, further comprising solvent processing at least a portion of the deasphalted oil fraction to form a Group I lubricant base stock.

Embodiment 9

[0081] The method of any of the above embodiments, further comprising fractionating at least a portion of the hydrotreated effluent to form a hydrotreated bottoms fraction and at least one of a naphtha boiling range fraction and a diesel boiling range fraction; deasphalting at least a portion of the hydrotreated bottoms fraction to form a hydrotreated deasphalted oil; and processing at least a portion of the hydrotreated deasphalted oil under fluid catalytic cracking conditions.

Embodiment 10

[0082] The method of Embodiment 9, wherein processing the at least a portion of the hydrotreated deasphalted oil under fluid catalytic cracking conditions further comprises processing a vacuum gas oil boiling range feed under the fluid catalytic cracking conditions.

Embodiment 11

[0083] The method of Embodiment 9 or 10, wherein processing the at least a portion of the hydrotreated deasphalted oil under fluid catalytic cracking conditions a) forms at least a catalytic slurry oil fraction, at least a portion of the catalytic slurry oil fraction being used as a co-feed for the hydrotreating of the deasphalter rock; b) forms at least a light cycle oil fraction having a final boiling point or T95 boiling point of about 650° F. (~343° C.) or less, at least a portion of the light cycle oil fraction being used as an aromatic solvent for the hydrotreating of the deasphalter rock; or c) a combination thereof.

Embodiment 12

[0084] The method of any of Embodiments 1 or 3-11, wherein performing solvent deasphalting on the resid feedstock comprises performing propane deasphalting on the resid feedstock.

Embodiment 13

[0085] The method of any of the above embodiments, wherein the deasphalter rock or the at least a portion of the deasphalter rock comprises at least about 10 wt % n-heptane insolubles, the hydrotreated effluent comprising about 50% or less of the n-heptane insolubles in the feedstock exposed to the fixed bed hydrotreating catalyst, or about 40% or less, or about 30% or less.

Embodiment 14

[0086] The method of any of the above embodiments, wherein the effective hydrotreating conditions are effective for conversion of at least about 40 wt % of the 1050° F.(566° C.) portion of the deasphalter rock or the at least a portion of the deasphalter rock, or at least about 50 wt %, or at least about 60 wt %, or at least about 65 wt %, or at least about 70 wt %, or wherein the effective hydrotreating conditions for conversion of the deasphalter rock comprise
a temperature of about 371° C. to about 433° C., optionally at least about 380° C. or at least about 399° C., or at least about 420° C., and a total pressure of about 600 psig (4.2 MPag) to about 6000 psig (42 MPag), optionally at least about 6.9 MPag or at least about 10.3 MPag, optionally about 34 MPag or less or about 28 MPag or less, or about 21 MPag or less, the effective hydropyrolyzing conditions optionally further comprising a hydrogen partial pressure of at least about 6.9 MPag or at least about 10.3 MPag and/or about 34 MPag or less or about 28 MPag or less or about 21 MPag or less; or a combination thereof.

Embodyment 15

[0087] The method of any of the above embodiments, further comprising hydrotreating of at least a portion of the deasphalted oil fraction, a combined conversion of the at least a portion of the deasphalted oil fraction and the (at least a portion of the) deasphalted rock fraction relative to 1050°F (566°C) being at least about 60 wt %, or at least about 70 wt %, or at least about 80 wt %, wherein optionally the hydrotreating conditions for the hydrotreating of the at least a portion of the deasphalted oil fraction comprise temperatures of 200°C to 430°C, or 315°C to 420°C; pressures of 250 psig (1.8 MPag) to 5000 psig (34.6 MPag) or 300 psig (2.1 MPag) to 3000 psig (20.8 MPag); liquid hourly space velocities (LHSV) of 0.1 hr⁻¹ to 10 hr⁻¹; and hydrogen treat rates of 200 scf/B (35.6 m³/m³) to 10,000 scf/B (1781 m³/m³), or 500 (89 m³/m³) to 5,000 scf/B (890 m³/m³).

Embodyment 16

[0088] The method of any of the above embodiments, wherein the hydrotreated effluent has a micro-carbon residue content that is about 50% or less of a micro-carbon residue content in the feedstock exposed to the fixed bed hydropyrolyzing catalyst, or about 40% or less, or about 30% or less; wherein the hydrotreated effluent has sulfur content of less than about 5000 ppm, or about 3000 ppm, or about 1000 ppm, and/or at least about 1 ppm, or at least about 100 ppm, or at least about 500 ppm or at least about 1000 ppm; or a combination thereof.

Embodyment 17

[0089] A hydrotreated effluent formed according to the method of any of the above embodiments.

EXAMPLES

Example of Reaction System Configuration

[0090] FIG. 1 schematically shows an example of a reaction system for processing deasphalted rock in a fixed bed hydropyrolyzing unit. In FIG. 1, an initial feed 105 that includes at least a portion of deasphalted rock can be introduced into a fixed bed hydropyrolyzing reactor (or reactors) 110. The initial feed 105 can also include a co-feed or an aromatic solvent. The hydrotreatment reactor(s) 110 can generate an effluent 115 that can be fractionated 120 to form any convenient number of products. As an example, the hydrotreated effluent 115 can be fractionated and/or separated 120 to form an H₂S output 121, a light ends (C₄₋₋₋) fraction 122, a light naphtha boiling range fraction (C₆₋₋₋₆₀° F.) 124, a diesel boiling range fraction (C₁₈₋₋₋₆₀° F.) 126, and a bottoms fraction 128. The bottoms fraction 128 can be deasphalted 130 to form a deasphalted oil 138 and a fraction containing asphalt and/or wax 139. Examples of suitable deasphalting methods can include pentane deasphalting and propane deasphalting.

[0091] FIG. 4 shows an example of integrating fixed bed hydropyrolyzing of deasphalted rock into a refinery process flow. In the example shown in FIG. 4, the fixed bed hydropyrolyzing of deasphalted rock is integrated with a fluid catalytic cracking (FCC) unit that can provide catalytic slurry oil as a co-feed as well as light cycle oil as an aromatic solvent.

[0092] In FIG. 4, a vacuum resid feed 445 is separated in a solvent deasphalt unit 440 to form a deasphalted oil 442 and deasphalted rock 405. The deasphalted rock 405 can be combined with an FCC bottoms fraction (catalytic slurry oil) 465 as a co-feed for hydrotreatment in a fixed bed hydrotreater 410. Optionally, if additional aromatic solvent is desired, a portion of light cycle oil (not shown) can also be added to the deasphalted rock 405 prior to hydrotreatment 410. The effluent 415 from hydrotreater 410 can optionally be combined with other feeds suitable for processing in an FCC reactor, such as a vacuum gas oil feed 454 or a portion 452 of the deasphalted oil 442. The hydrotreated effluent 415 can then be processed in FCC reactor 460 to form FCC bottoms fraction 465 and a plurality of lower boiling products 468. Any remaining portion of deasphalted oil 442 can, for example, be processed in a Group I tubular plant 470 to form a plurality of products, such as an aromatic extract product 471, a Group I base stock product 473, and a wax product 475.

Example 1

Fixed Bed Hydropyrolyzing of Deasphalted Rock with Xylene Solvent

[0093] A deasphalted rock feed was formed by performing solvent deasphaltation of a vacuum resid in a ROSE unit. The resulting deasphalted rock had a density of 1.10 g/cm³, 6 wt % sulfur, 0.7 wt % nitrogen, 40 wt % micro-carbon residue, 92 wppm Ni, and 304 wppm V. The rock is about 6 wt % 650°F-1050°F and about 94 wt % greater than 1050°F. At room temperature the rock was a brittle solid. In order to form a liquid feed, the rock was dissolved in xylene to produce a feed corresponding to about 60 wt % rock and 40 wt % xylene.

[0094] A fixed bed reactor was loaded with crushed extrudates (40-60 mesh) of a commercially available supported CoMo catalyst. The mixture of feed and solvent was processed at 400°C, 1000 psig, 6000 SCF/B, and 0.08 WHSV. The reaction configuration roughly corresponded to the configuration shown in FIG. 1. The reaction system was operated for about 200 days to identify any potential deactivation of the catalyst at long processing run times. The composition of the hydrotreated effluent was relatively stable from about day 80 to about 200 of the processing run. A material balance for the fixed bed hydropyrolyzing of the deasphalted rock (not including the xylene solvent) is also shown in FIG. 1. The material balance shown in FIG. 1 is based on cut points between C₄ and C₅, between C₆ and C₁₀, and at 600°F (316°C). The material balance can also be expressed based on a naphtha boiling range of about C₆ to 350°F (177°C), 350°F to 650°F (343°C), and 650°F-1050°F (566°C). Based on this second definition for describing the material balance, the hydrotreated effluent
during the course of the processing run included about 4.5 wt % H₂S, about 4 wt % light ends (C₃–), about 7 wt % naphtha, about 15 wt % 350° F-650° F. (diesel), about 32 wt % 650° F-1050° F., and about 37 wt % 1050° F+. Based on the initial feed, this corresponds to between about 55% and 60% conversion relative to 1050° F.

[0095] FIG. 2 shows a further comparison of the composition of the hydrotreated effluent relative to the initial deasphalter rock feed. In FIG. 2, the abbreviation “ARC” refers to the number of aromatic rings in a compound. The last 4 categories include two bars, with the left bar corresponding to the feed while the right bar corresponds to the hydrotreated product. As shown in FIG. 2, the initial feed based on the deasphalter rock includes only 4+ ring aromatics, sulfides, polar compounds, and solids. After hydrotreatment of the feed in FIG. 2, the about 80 wt % solids in the deasphalter rock feed have been reduced to about 18 wt % solids in the hydrotreated effluent.

[0096] During the stable portion of the processing run, the fixed bed hydrotreatment removed about 75 wt %-80 wt % of the sulfur and about 80 wt % of the metals (Ni+V). As shown in FIG. 3, the hydrotreatment also resulted in an increase in API gravity for the hydrotreated effluent relative to the deasphalter rock that started at about 12 and then settled at about 8 during the stable portion of the processing run. This long term stability of the fixed bed hydrotreatment process was unexpected based on the nature of the feed. It is noted that the observed loss in activity in FIG. 3 appears to be due to deposition of metals on the catalyst, rather than accumulation of coke.

[0097] In a typical fixed bed process for treating a vacuum resid, a WHSV of about 0.1 hr⁻¹ would be used under conditions suitable for conversion of about 40-55% of the feed relative to 1050° F. Thus, about 10,000 barrels of catalyst are needed for each 1000 barrels/hr of feed. The process run length for conventional resid hydrousprocessing can be determined based on accumulation of metals, with a conventional run end point when about 15 wt % to about 20 wt % of metals are deposited on the catalyst.

[0098] By contrast, by processing the rock portion of a feed separately from the remaining deasphalted oil portion of a resid, higher net space velocities can be achieved while also achieving both greater conversion and longer run length. A typical rock yield from propane deasphalting can be about 40 wt % of a resid feed. The resulting deasphalted oil can be processed at about 0.5 hr⁻¹ WHSV (about 1200 barrels of catalyst per 1000 barrels/hour) while the deasphalter rock can be processed at about 0.05 hr⁻¹ (about 8000 barrels of catalyst per 1000 barrels/hour). The amount of combined conversion for processing of both feeds can be about 80% to about 85%. The deasphalted oil can have a low metals content and low coke formation on catalyst, allowing for extended run length. The deasphalter rock can also have an extended run length. Due to the reduced or minimized coke formation, the run length for processing the deasphalter rock can instead be based on metals accumulation. The amount of metal accumulation while maintaining desired catalyst activity can be about 20 wt % to about 30 wt %, due to the reduced or minimized amount of coke deposition. Based on the reduced catalyst amount and the extended run length between catalyst change, performing fixed bed processing separately on deasphalter rock and deasphalted oil can reduce catalyst consumption by about 20% to about 50% relative to conventional resid processing.

Example 2

Example of Integration with Refinery Processing

[0099] A process train similar to the configuration shown in FIG. 4 was used to process a vacuum resid feed. The initial vacuum resid feed had an API Gravity of about 4.9, a sulfur content of about 5.4 wt %, a micro-carbon residue content of about 22.3 wt %, a nitrogen content of about 0.3 wt %, and a metals content (Ni+V) of about 200 wppm. The solubility number for the vacuum resid was about 100 and the insolubility number was about 25.

[0100] The vacuum resid feed was commercially deasphalted by propane deasphalting to form a deasphalted oil and deasphalter rock. The deasphalted oil had an API gravity of about 1%, a sulfur content of about 3.05 wt %, a microcarbon residue content of about 2.4 wt %, a nitrogen content of about 0.1 wt %, a solubility number of 40, and an insolubility number of 0. The deasphalted oil had little or no content of Ni and/or V. The deasphalted oil was suitable for further processing, such as in a Group I lube plant or in a fluid catalytic cracking process. The deasphalter rock had an API gravity of about 0.6, a sulfur content of about 6.3 wt %, a micro-carbon residue of about 30.2 wt %, a nitrogen content of about 0.22 wt %, a metals content (Ni+V) of about 225 wppm, a solubility number of about 125, and an insolubility number of about 25.

[0101] The deasphalter rock was used to form a feed by combining 60 wt % of deasphalter rock with 40 wt % of a catalytic slurry oil. The catalytic slurry oil had an API gravity of about -5.0, a sulfur content of about 3.9 wt %, a micro-carbon residue of about 9.5 wt %, a nitrogen content of about 0.18 wt %, a solubility number of about 200, and an insolubility number of about 87. The combined deasphalter rock and catalytic slurry oil feed was processed at 2500 psig (17 MPag), 400° C., and 0.2 LHSV over a commercially available supported CoMo hydrotreating catalyst. The effluent from hydrousprocessing of the deasphalter rock and co-feed had a sulfur content of about 0.1 wt %, a micro-carbon residue of about 1 wt %, an API gravity of about 19, and a nitrogen content of about 0.05 wt %. About 20 wt % of the effluent had a boiling point greater than 1050° F. This effluent was suitable for use as part of a feed to a fluid catalytic cracking unit.

[0102] FIG. 4 shows an example of how the hydrotreated oil effluent from treating a combination of deasphalter rock and catalytic slurry oil can be integrated with an overall refinery scheme. As shown in FIG. 4, the hydrotreated effluent from treating the deasphalter rock/catalytic slurry oil feed can be combined with additional vacuum gas oil to serve as a feed for a commercial scale FCC reactor. The FCC process can generate the catalytic slurry oil used as co-feed for the deasphalter rock. If the amount of catalytic slurry oil is not sufficient, light cycle oil from the FCC process can be used as an aromatic solvent, in an amount corresponding to up to about 50 wt % of the feed. The deasphalted oil can be used for Group I lube production and/or as additional vacuum gas oil for FCC processing.

[0103] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the invention 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
invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

The present invention has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

What is claimed is:

1. A method for fixed bed processing of deasphalter rock, comprising:
   - exposing a feedstock comprising deasphalter rock and a co-feed comprising a catalytic slurry oil, a lubes extract, a heavy coker gas oil, a vacuum gas oil derived from a heavy oil, or a combination thereof, to a fixed bed of hydroprocessing catalyst under hydroprocessing conditions effective for conversion of at least 40 wt % of the deasphalter rock relative to a conversion temperature of 1650°F (849°C) to form a hydroprocessed effluent, the feedstock comprising at least about 20 wt % of the co-feed and at least about 10 wt % of the deasphalter rock.

2. The method of claim 1, wherein the feedstock comprises at least about 30 wt % of the deasphalter rock.

3. The method of claim 1, further comprising performing solvent deasphalting on a resid feedstock to form at least the deasphalter rock and a deasphalted oil fraction, the resid feedstock having a T10 distillation point of at least about 650°F (−343°C), the deasphalter rock comprising at least about 10 wt % of the resid feedstock.

4. The method of claim 1, wherein the feedstock comprises at least about 20 wt % of the catalytic slurry oil.

5. The method of claim 1, wherein the feedstock comprises at least about 30 wt % of the co-feed.

6. The method of claim 1, wherein the feedstock further comprises an aromatic solvent, the aromatic comprising at least 50 wt % of aromatic compounds relative to a weight of the aromatic solvent, the aromatic solvent having a boiling range from about 100°C to about 500°C.

7. The method of claim 6, wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 300°C, or less, or wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 350°C, or less and the feedstock comprises about 40 wt % or less of the aromatic solvent, or wherein the aromatic solvent has a final boiling point of a T95 boiling point of about 400°C, or less and the feedstock comprises about 30 wt % or less of the aromatic solvent.

8. The method of claim 1, further comprising fractionating at least a portion of the hydroprocessed effluent to form a hydroprocessed bottoms fraction and at least one of a naphtha boiling range fraction and a diesel boiling range fraction; deasphalting at least a portion of the hydroprocessed bottoms fraction to form a hydroprocessed deasphalted oil; and processing at least a portion of the hydroprocessed deasphalted oil under fluid catalytic cracking conditions.

9. The method of claim 8, wherein processing the at least a portion of the hydroprocessed deasphalted oil under fluid catalytic cracking conditions further comprises processing a vacuum gas oil boiling range feed under the fluid catalytic cracking conditions.

10. The method of claim 8, wherein processing the at least a portion of the hydroprocessed deasphalted oil under fluid catalytic cracking conditions forms at least a catalytic slurry oil fraction, at least a portion of the catalytic slurry oil fraction being used as the co-feed for the hydroprocessing of the deasphalter rock.

11. The method of claim 8, wherein processing the at least a portion of the hydroprocessed deasphalted oil under fluid catalytic cracking conditions forms at least a light cycle oil fraction having a final boiling point or T95 boiling point of about 650°F (−343°C) or less, at least a portion of the light cycle oil fraction being used as an aromatic solvent for the hydroprocessing of the deasphalter rock.

12. The method of claim 1, wherein the deasphalter rock comprises at least about 10 wt % n-heptane insolubles, the hydroprocessed effluent comprising about 50% or less of the n-heptane insolubles in the feedstock exposed to the fixed bed hydroprocessing catalyst.

13. The method of claim 1, wherein the effective hydroprocessing conditions are effective for conversion of at least about 40 wt % of the 1050°F (+566°C) portion of the deasphalter rock.

14. The method of claim 1, wherein the effective hydroprocessing conditions for conversion of the deasphalter rock comprise a temperature of about 371°C to about 433°C and a total pressure of about 600 psig (4.2 MPag) to about 6000 psig (42 MPag).

15. The method of claim 1, further comprising hydrotreatment of at least a portion of the deasphalted oil fraction, a combined conversion of the at least a portion of the deasphalted oil fraction and the (at least a portion of the) deasphalter rock fraction relative to 1050°F (566°C) being at least about 60 wt %.

16. The method of claim 1, wherein the hydroprocessed effluent has a micro-carbon residue content that is about 50% or less of a micro-carbon residue content in the feedstock exposed to the fixed bed hydroprocessing catalyst.

17. A method for fixed bed processing of deasphalter rock, comprising:
   - performing solvent deasphalting on a resid feedstock to form a deasphalter rock fraction and a deasphalted oil fraction, the resid feedstock having a T10 distillation point of at least about 650°F (−343°C), the deasphalter rock fraction comprising at least about 10 wt % of the resid feedstock; and
   - exposing a feedstock comprising at least a portion of the deasphalter rock fraction to a fixed bed of hydroprocessing catalyst under hydroprocessing conditions effective for conversion of at least 40 wt % of the at least a portion of the deasphalter rock relative to a conversion temperature of 1050°F (566°C) to form a hydroprocessed effluent, the feedstock comprising at least about 10 wt % of the at least a portion of the deasphalter rock.

18. The method of claim 17, wherein performing solvent deasphalting on the resid feedstock comprises performing propane deasphalting on the resid feedstock.

19. The method of claim 17, further comprising solvent processing at least a portion of the deasphalted oil fraction to form a Group I lubricant base stock.
20. A hydrotreated effluent formed from processing of deasphalter rock, the hydrotreated effluent formed by the method comprising:
exposing a feedstock comprising deasphalter rock and a co-feed comprising a catalytic slurry oil, a lubes extract, a heavy coker gas oil, a vacuum gas oil derived from a heavy oil, or a combination thereof, to a fixed bed of hydrosprocessing catalyst under hydrosprocessing conditions effective for conversion of at least 40 wt % of the deasphalter rock relative to a conversion temperature of 1060°F (566°C) to form a hydrosprocessed effluent, the feedstock comprising at least about 20 wt % of the co-feed and at least about 10 wt % of the deasphalter rock.