(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 June 2016 (30.06.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/106228 A1

(51) International Patent Classification:
C10G 11/00 (2006.01) *C10G 31/00* (2006.01)

(21) International Application Number:
PCT/US2015/067132

(22) International Filing Date:
21 December 2015 (21.12.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/095,926 23 December 2014 (23.12.2014) US

(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 The Hague (NL).

(72) Inventors: **POWELL, Joseph Broun**; 10506 Normont Drive, Houston, Texas 77070 (US). **TSAI, Kuochen**; 6410 Dylan Springs Lane, Katy, Texas 77450 (US). **SOTHEN, Ryan Anthony**; 3906 Floyd St., Houston, Texas 77007 (US). **STEPHENS, Ryan Mark**; 14115 Edinburgh Court, Houston, Texas 77077 (US). **BEJ, Shyamal K**; 2100 Welch St. # C111, Houston, Texas 77019 (US). **PHALAK, Nihar**; 15135 Memorial Dr. #6110, Houston, Texas 77079 (US). **CHIKYALA, Vikramaditya**; 27211 Walden Gulch Lane, Katy, Texas 77494 (US). **BOS, Alouisius Nicolaas Renée**; Grasweg 31, 1031HW Amsterdam (NL).

(74) Agent: **TAYLOR, Richard B.**; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,

[Continued on next page]

(54) Title: PROCESS FOR TREATING A HYDROCARBON-CONTAINING FEED

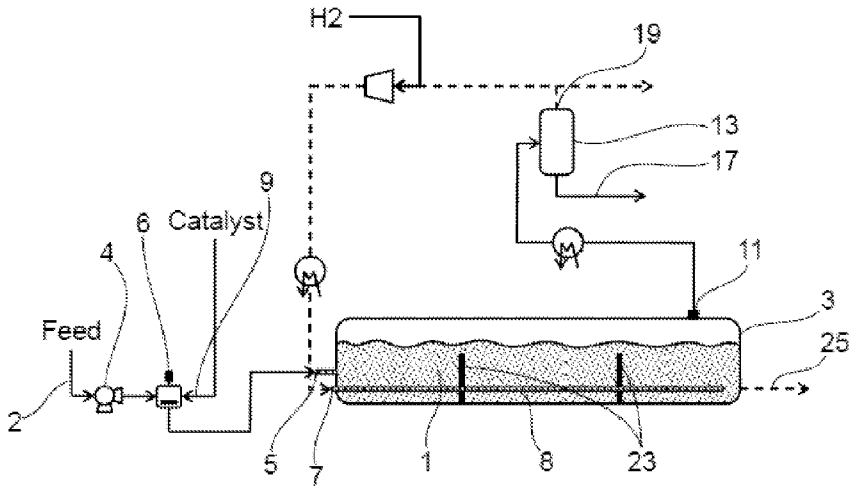

FIG. 1

(57) Abstract: A process for hydroprocessing a hydrocarbon feedstock. The process utilizes a horizontal bubble reactor for slurry hydroprocessing of a heavy hydrocarbon feedstock having an API Gravity of less than 20, where the reactor is fitted with one or more vapor-only outlets to provide intrinsic separation of catalyst from product.

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LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

PROCESS FOR TREATING A HYDROCARBON-CONTAINING FEED

Cross Reference to Related Applications

[0001] This application claims the benefit of U. S. Provisional Application No. 62/095,926, filed on December 23, 2014, which is incorporated herein by reference.

Field

[0002] The present disclosure is directed to a process for treating a hydrocarbon-containing feedstock. More particularly, the present disclosure is directed to a slurry process for hydrotreating a hydrocarbon-containing feedstock.

Background

[0003] Increasingly, resources such as heavy crude oils, bitumen, tar sands, shale oils, and hydrocarbons derived from liquefying coal are being utilized as hydrocarbon sources due to decreasing availability of easily accessed light sweet crude oil reservoirs. These resources are disadvantaged relative to light sweet crude oils, as they contain significant amounts of heavy hydrocarbon fractions such as residue and asphaltenes, and often contain significant amounts of sulfur, nitrogen, metals, and/or naphthenic acids. The disadvantaged crudes typically require a considerable amount of upgrading, for example by hydrotreating and by cracking, in order to obtain more valuable hydrocarbon products. Upgrading by cracking, either thermal cracking, hydrocracking and/or catalytic cracking, is also effective to partially convert heavy hydrocarbon fractions such as atmospheric or vacuum residues derived from refining a crude oil or hydrocarbons derived from liquefying coal into lighter, more valuable hydrocarbons.

[0004] Numerous processes have been developed to crack and treat disadvantaged crude oils and heavy hydrocarbon fractions to recover lighter hydrocarbons and to reduce metals, sulfur, nitrogen, and acidity of the hydrocarbon-containing material. For example, a hydrocarbon-containing feedstock may be hydrotreated and/or cracked by passing the hydrocarbon-containing feedstock over a catalyst located in a fixed bed catalyst reactor in the presence of hydrogen at a temperature effective to reduce the sulfur content, nitrogen content, metals content, and/or the acidity of the feedstock and/or crack heavy hydrocarbons in the feedstock. Another method to hydrotreat and/or crack a hydrocarbon-containing feedstock is to disperse a catalyst in the feedstock and pass the feedstock and

catalyst together with hydrogen through a slurry-bed or fluid-bed reactor operated at a temperature effective to reduce the sulfur content, nitrogen content, metals content, and/or the acidity of the feedstock and/or crack heavy hydrocarbons in the feedstock. Examples of such slurry-bed or fluid-bed reactors include ebullating-bed reactors, plug-flow reactors, and bubble-column reactors.

[0005] Coke formation, however, is a particular problem in processes for hydrotreating or cracking a hydrocarbon-containing feedstock having a relatively large amount of heavy hydrocarbons such as residue and asphaltenes. Substantial amounts of coke are formed in current processes for hydrotreating/cracking heavy hydrocarbon-containing feedstocks, limiting the yield of lighter molecular weight hydrocarbons that can be recovered and decreasing the efficiency of the process by limiting the extent of hydrocarbon conversion that can be effected in the process, for example, by deactivating the catalyst used in the process.

[0006] Hydrocarbon-containing feedstocks having a relatively high concentration of heavy hydrocarbon molecules therein are particularly susceptible to coking due to the presence of a large quantity of high molecular weight hydrocarbons in the feedstock with which cracked hydrocarbon radicals may combine to form proto-coke or coke. As a result, hydrotreating processes of heavy hydrocarbon-containing feedstocks have been limited by coke formation induced at least in part by the cracking reaction itself.

[0007] Slurry catalyst processes have been utilized to address the problem of catalyst aging by coke deposition in the course of cracking a hydrocarbon-containing feedstock. Slurry catalyst particles are selected to be dispersible in the hydrocarbon-containing feedstock so that the slurry catalyst circulates with the hydrocarbon-containing feedstock in the course of the cracking reaction. The feedstock and the catalyst move together through the reactor and are separated after exiting the cracking reactor. Coke formed during the cracking reaction is separated from the product, and any coke deposited on the catalyst may be removed from the catalyst by regeneration of the catalyst.

[0008] Improved processes for hydrotreating and cracking heavy hydrocarbon-containing feedstocks are desirable, particularly those having fewer reaction and separation steps, improved yields, reduced scale-up risks, and in which coke formation is significantly reduced.

Summary

[0009] In one aspect, provided herein is a slurry process for conversion of a hydrocarbon feedstock. The process comprises the following steps:

introducing a hydrocarbon feedstock having an API Gravity of less than 20, a solid particulate hydrotreating catalyst capable of activating molecular hydrogen, and hydrogen gas into a horizontal reactor having a length that is greater than its height, wherein the reactor is fitted with one or more separate vapor-only outlets, and further wherein the hydrogen gas is introduced into the horizontal reactor as bubbles to a mixture of the hydrocarbon feedstock and the solid hydrotreating catalyst;

contacting the hydrocarbon feedstock-solid hydrotreating catalyst mixture and the bubbles of hydrogen gas at a temperature of from 375°C to 550°C and a total pressure of at least 2 MPa to thereby produce a vapor product and a liquid hydrocarbon-depleted residuum, optionally with the formation of a coke byproduct, and optionally with the formation of a metals byproduct;

removing the vapor product from the horizontal reactor through the one or more separate vapor-only outlet locations downstream from a hydrocarbon feedstock inlet along the length of the horizontal reactor, and

removing the liquid hydrocarbon-depleted residuum, catalyst solids, optional coke byproduct, and optional metals byproduct from the reactor from one or more purge zones downstream from the hydrocarbon feedstock inlet along the length of the horizontal reactor.

[0010] Additional embodiments of the process, reactor configurations, post-processing steps, and the like will be apparent from the following description, examples, and claims. As can be appreciated from the foregoing and following description, each and every feature described herein, and each and every combination of two or more of such features, is included within the scope of the present disclosure provided that the features included in such a combination are not mutually inconsistent. In addition, any feature or combination of features may be specifically excluded from any embodiment of the present invention. Additional aspects and advantages of the present invention are set forth in the following description, particularly when considered in conjunction with the accompanying examples and drawings.

Brief Description of the Drawings

[0011] Fig. 1 is a schematic of an exemplary system useful for practicing the process provided herein.

[0012] Fig. 2 is a schematic of a system demonstrating optional differential separation of products from the conversion process provided herein.

[0013] Fig. 3 is a schematic of another embodiment of a system demonstrating optional differential separation of products from the conversion process provided herein.

[0014] Fig. 4 is a simplified schematic representation of a conversion process as described herein.

[0015] Fig. 5 is a schematic of an embodiment of a system useful for practicing the process provided herein.

[0016] Fig. 6 is a schematic of an embodiment of a system useful for practicing the process provided herein.

Detailed Description

[0017] The present disclosure is directed to a process for hydroprocessing a hydrocarbon feedstock. The process utilizes a horizontal bubble reactor for slurry hydroprocessing of a heavy hydrocarbon feedstock having an API Gravity of less than 20. The reactor is fitted with one or more vapor outlets to provide intrinsic separation of catalyst from product. Utilization of a horizontal reactor allows the entire cross section of the reactor to function as a gas disengagement zone. The vapor product, after removal from the reactor, may be further cooled and condensed to provide liquid products having, for example, reduced viscosity, a reduced metals content, a reduced sulfur and nitrogen content, a higher hydrogen to carbon ratio, a lower amount of asphaltenes, and the like, relative to the heavy hydrocarbon feedstock, which may then be further processed to provide liquid fuels and chemicals.

[0018] Generally, a process is provided for conversion of a heavy hydrocarbon feedstock. The process comprises the steps of:

(a) introducing a hydrocarbon feedstock having an API Gravity of less than 20, a solid particulate hydrotreating catalyst capable of activating molecular hydrogen, and hydrogen gas into a horizontal reactor having a length that is greater than its height,

wherein the reactor is fitted with one or more separate vapor-only outlets and has one or more stages, and further wherein the hydrogen gas is introduced into the horizontal reactor as bubbles to the hydrocarbon feedstock,

(b) contacting the hydrocarbon feedstock, the hydrotreating catalyst, and the bubbles of hydrogen gas at a temperature of from 375°C to 550°C and a total pressure of at least 2 MPa to thereby produce a vapor product and a hydrocarbon-depleted residuum, optionally with the formation of a coke byproduct and optionally with formation of a metals byproduct,

(c) removing the vapor product from the horizontal reactor through the one or more separate vapor-only outlet locations located downstream along the length of the horizontal reactor from a hydrocarbon feedstock inlet, and

(d) removing the liquid hydrocarbon-depleted residuum, catalyst solids, optional coke byproduct, and optional metals byproduct from the reactor from one or more purge zones located downstream along the length of the horizontal reactor from the hydrocarbon feedstock inlet.

[0019] Current industrial slurry hydroprocessing processes result in solids (e.g., catalyst and coke)-containing liquid hydrocarbon product streams exiting the reactor. The streams are depressurized, and the solids along with unconverted liquid products are circulated through distillation columns, followed by either solvent deasphalting for catalyst recycle, or by a physical separation step to remove catalyst and coke, followed by regeneration and recirculation of the catalyst via an external process loop. Processes such as these, requiring external solids circulation, are at increased risk for pipe erosion, and often suffer from operability and performance reliability issues due to the solids processing steps. In contrast to the foregoing, the current process, rather than separating light hydrocarbon products from unconverted heavy hydrocarbon products subsequent to hydroprocessing, allows hydrocarbons having a boiling point of less than 538°C, for example naphtha, kerosene, diesel and VGO hydrocarbons, to be stripped from the horizontal reactor in the hydrotreatment process, leaving the slurry catalyst, a liquid hydrocarbon-depleted residuum, optionally petroleum-coke byproduct, and optionally a metals byproduct containing iron, vanadium, and nickel behind in the reactor. Separation of a majority (greater than 90%, preferably greater than 95%) of desired product as a vapor from liquid residuum, coke solids, slurry catalyst and metals occurs easily in the reactor. External

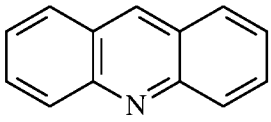
recovery and recycle of the catalyst is not required, nor are separate distillation steps required to separate vapor from unreacted liquid hydrocarbon-depleted residuum. Separation of the hydrocarbon product as a vapor over the length of the horizontal reactor allows for substantially all light hydrocarbon products to be stripped from the horizontal reactor as vapor. The vapor is then cooled and condensed to provide liquid hydrocarbon products of reduced viscosity and metals content, which can then be further refined to liquid fuels and chemicals.

[0020] One major concern of slurry processing, especially upon scale-up, is the potential for gas bubble coalescence. Bubble coalescence is more likely to occur at high solids concentrations within the reactor, particularly when the height of liquid within the column is great. Bubble coalescence leads to the formation of larger gas bubbles, where the larger gas bubbles have a higher rise velocity than smaller-sized bubbles within the column, thereby potentially leading to rapid foam formation and carry-out of feed from the reactor. In addition, large gas bubbles are less effective in creating interfacial area for transport of hydrogen into the liquid phase, than an ensemble of smaller bubbles. Maintenance of smaller bubbles for effective hydrogen transport into the liquid phase, for effective suppression of coke forming reactions, is a key aspect of the current invention. In the instant process provided herein, it is believed that the use of a high volumetric flow rate of hydrogen, from 800 Nm^3 (hydrogen)/m^3 (feedstock) to 4000 Nm^3(hydrogen)/m^3(feedstock), at a relatively low linear velocity hydrogen flow rate, less than 7 ft/min (1400 m/hr), or from 0.05 ft/min (10 m/hr) to 1 ft/min (200 m/hr), or from 0.1 ft/min (20 m/hr) to 0.5 ft/min (100 m/hr), allows for substantially all volatile hydrocarbon products to be stripped from the reactor without entraining liquid from the reactor in the vapor product separated from the reactor. In order to operate at such a high volumetric flow rate of hydrogen, the process utilizes a horizontal reactor to thereby provide a reduction of the linear velocity of the gas, such that liquid foam out of the reactor and unstable turbulence are avoided despite the high volume gas flowrates required for stripping of product. The use of a horizontal reactor for the instant process further allows for features such as crossflow stripping and a reduced propensity for gas bubble coalescence by providing shorter distances for gas coalescence relative to a vertical reactor.

[0021] Further details and advantages of the process are described in the sections which follow.

[0022] Certain terms that are used herein are defined as set forth below:

[0023] "Acridinic compound" refers to a hydrocarbon compound that comprises the following acridine core structure:



including compounds comprising the fused 3-ring structure shown above, but optionally substituted at any one or more of carbon positions 1-9 in the ring system or at the nitrogen atom. As used in the present application, an acridinic compound includes any hydrocarbon compound containing the above structure, including, naphthenic acridines, napththenic benzoacridines, and benzoacridines, in addition to acridine.

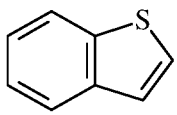
[0024] "Aqueous" as used herein is defined as containing more than 50 vol.% water. For example, an aqueous solution or aqueous mixture, as used herein, contains more than 50 vol.% water.

[0025] "ASTM" refers to American Standard Testing and Materials.

[0026] "Atomic hydrogen percentage" and "atomic carbon percentage" of a hydrocarbon-containing material—including crude oils, crude products such as syncrudes, bitumen, tar sands hydrocarbons, shale oil, crude oil atmospheric residues, crude oil vacuum residues, naphtha, kerosene, diesel, VGO, and hydrocarbons derived from liquefying coal-are as determined by ASTM Method D5291.

[0027] "API Gravity" refers to API Gravity at 15.5°C, and as determined by ASTM Method D6822.

[0028] "Benzothiophenic compound" refers to a hydrocarbon compound including the structure:



As used in the present application, a benzothiophenic compound includes any hydrocarbon compound containing the above structure, including di-benzothiophenes, naphthenic-

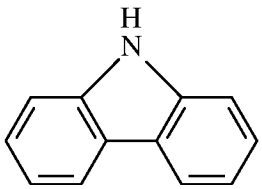
benzothiophenes, napththenic-di-benzothiophenes, benzo-naphtho-thiophenes, naphthenic-benzo-naphthothiophenes, and dinaphtho-thiophenes, in addition to benzothiophene.

[0029] "BET surface area" refers to a surface area of a material as determined by ASTM Method D3663.

[0030] "Blending" as used herein is defined to mean contact of two or more substances by intimately admixing the two or more substances.

[0031] Boiling range distributions for a hydrocarbon-containing material are as determined by ASTM Method D5307.

[0032] "Carbazolic compound" refers to a hydrocarbon compound including the structure:



As used in the present application, a carbazolic compound includes any hydrocarbon compound containing the above structure, including naphthenic carbazoles, benzocarbazoles, and napthenic benzocarbazoles, in addition to carbazole.

[0033] "Carbon number" refers to the total number of carbon atoms in a molecule.

[0034] "Catalyst" refers to a substance that increases the rate of a chemical process and/or that modifies the selectivity of a chemical process as between potential products of the chemical process, where the substance is not consumed by the process. A catalyst, as used herein, may increase the rate of a chemical process by reducing the activation energy required to effect the chemical process. Alternatively, a catalyst, as used herein, may increase the rate of a chemical process by modifying the selectivity of the process between potential products of the chemical process, which may increase the rate of the chemical process by affecting the equilibrium balance of the process. Further, a catalyst, as used herein, may not increase the rate of reactivity of a chemical process but merely may modify the selectivity of the process as between potential products.

[0035] "Coke" is a solid carbonaceous material that is formed primarily of a hydrocarbonaceous material and that is insoluble in toluene as determined by ASTM Method D4072.

[0036] "Cracking" as used herein with reference to a hydrocarbon-containing material refers to breaking hydrocarbon molecules in the hydrocarbon-containing material into hydrocarbon fragments, where the hydrocarbon fragments have a lower molecular weight than the hydrocarbon molecule from which they are derived. Cracking effected by temperature rather than by the presence of hydrogen or the presence of a catalyst may be referred to as thermal cracking.

[0037] "Diesel" refers to hydrocarbons with a boiling range distribution from 260°C up to 343°C (500°F up to 650°F) at a pressure of 0.101 MPa. Diesel content may be determined by the quantity of hydrocarbons having a boiling range of from 260°C to 343°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

[0038] "Distillate" or "middle distillate" refers to hydrocarbons with a boiling range distribution from 204°C up to 343°C (400°F up to 650°F) at a pressure of 0.101 MPa. Distillate content is as determined by ASTM Method D5307. Distillate may include diesel and kerosene.

[0039] A "horizontal reactor" refers to a reactor having a horizontal dimension that is greater than its vertical dimension. The length to diameter ratio of the horizontal reactor is at least 3, or from 3-50, or from 4-36, or from 6-12. An upper surface of a horizontal reactor refers to a surface above the midline of the reactor, generally falling within 20% of the uppermost surface area of the reactor determined from the midline of the reactor upwards towards the apex. A lower surface of a horizontal reactor refers to a surface below the midline of the reactor, generally falling within 20% of the lowermost surface area of the reactor determined from the midline of the reactor downward towards the lowest point.

[0040] "Hydrogen" as used herein refers to molecular hydrogen unless specified as atomic hydrogen.

[0041] "Insoluble" as used herein refers to a substance a majority (at least 50 wt.%) of which does not dissolve or disperse in a liquid after a period of 24 hours upon being mixed with the liquid at a specified temperature and pressure, where the undissolved portion of the substance can be recovered from the liquid by physical means. For example, a fine particulate material dispersed in a liquid is insoluble in the liquid if 50 wt.% or more of the material may be recovered from the liquid by centrifugation and filtration.

[0042] "Kerosene" refers to hydrocarbons with a boiling range distribution from 204°C up to 260°C (400°F up to 500°F) at a pressure of 0.101 MPa. Kerosene content may be determined by the quantity of hydrocarbons having a boiling range of from 204°C to 260°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

[0043] "Light hydrocarbons" refers to hydrocarbons having carbon numbers in a range from 1 to 6.

[0044] "Mixing" as used herein is defined as contacting two or more substances by intermingling the two or more substances. Blending, as used herein, is a subclass of mixing, where blending requires intimately admixing or intimately intermingling the two or more substances, for example into a homogenous dispersion.

[0045] "Naphtha" refers to hydrocarbon components with a boiling range distribution from 38°C up to 204°C (100°F up to 400°F) at a pressure of 0.101 MPa. Naphtha content may be determined by the quantity of hydrocarbons having a boiling range of from 38°C to 204°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

[0046] When two or more elements are described as "operatively connected", the elements are defined to be directly or indirectly connected to allow direct or indirect fluid flow between the elements.

[0047] "Periodic Table" refers to the Periodic Table as specified by the International Union of Pure and Applied Chemistry (IUPAC), November 2003. As used herein, an element of the Periodic Table of Elements may be referred to by its symbol in the Periodic

Table. For example, Cu may be used to refer to copper, Ag may be used to refer to silver, W may be used to refer to tungsten etc.

[0048] "Polyaromatic compounds" refer to compounds that include two or more aromatic rings. Examples of polyaromatic compounds include, but are not limited to, indene, naphthalene, anthracene, phenanthrene, benzothiophene, dibenzothiophene, and bi-phenyl.

[0049] "Pore size distribution" refers a distribution of pore size diameters of a material as measured by ASTM Method D4641.

[0050] "Residue" refers to components that have a boiling range distribution above 538 °C (1000 °F) at 0.101 MPa, as determined by ASTM Method D5307.

[0051] "SCFB" refers to standard cubic feet of gas per barrel of crude feed.

[0052] "STP" as used herein refers to Standard Temperature and Pressure, which is 25°C and 0.101 MPa.

[0053] The term "substantially" in reference to a certain feature such as conversion means to a significant degree or nearly completely (i.e. to a degree of 90% or greater) in reference to the feature or entity.

[0054] "VGO" refers to hydrocarbons with a boiling range distribution of from 343°C up to 538°C (650°F up to 1000°F) at 0.101 MPa. VGO content may be determined by the quantity of hydrocarbons having a boiling range of from 343°C to 538°C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307.

[0055] The term, "wppm", as used herein refers to parts per million, by weight.

[0056] The present disclosure is directed to a slurry process for conversion of a hydrocarbon-containing feedstock in which the hydrocarbon-containing feedstock, hydrogen, and a catalyst capable of activating hydrogen are mixed at a temperature of from 375°C to 550°C and a total pressure of at least 2.0 MPa, preferably a hydrogen partial pressure of at least 2.0 MPa, in a horizontal reactor to provide a vapor comprising a hydrocarbon-containing product comprising one or more hydrocarbon compounds that are

liquid at STP, where the vapor can be separated from the horizontal reactor substantially absent or free of any solids or liquid hydrocarbon-depleted resdiuum. The hydrogen gas is introduced as bubbles to the hydrocarbon-containing feedstock, and the vapor is removed from the reactor through one or more vapor-only outlets. Components of the process are described below.

Hydrocarbon-containing feedstock

[0057] The hydrocarbon-containing feedstock contains heavy hydrocarbons that are subject to being cracked in the hydrotreating process. The hydrocarbon-containing feedstock possesses an API Gravity of less than 20, as determined in accordance with ASTM Method D287. The hydrocarbon-containing feedstock may have an API Gravity selected from, for example, less than 20, or less than 18, or less than 16, or even less than 15. A hydrocarbon-containing feedstock may be selected to possess an API Gravity from 3-15, or from 3-12, or from 3-10, or from 4-9. The hydrocarbon-containing feedstock may also be selected to contain at least 20 wt.% residue, or at least 25 wt.% residue, or at least 30 wt.% residue, or at least 35 wt.% residue, or at least 40 wt.% residue, or at least 45 wt.% residue, or least 50 wt.% residue.

[0058] The hydrocarbon-containing feedstock may contain significant quantities of lighter hydrocarbons as well as the heavy hydrocarbons. The hydrocarbon-containing feedstock may contain at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.%, or at least 45 wt.%, or at least 50 wt.% of hydrocarbons having a boiling point of 538°C or less as measured at a pressure of 0.101 MPa. The amount of hydrocarbons having a boiling point of 538°C or less in a hydrocarbon-containing material may be determined in accordance with ASTM Method D5307. The hydrocarbon-containing feedstock may contain at least 20 wt.%, or at least 25 wt.%, or at least 30 wt.%, or at least 35 wt.%, or at least 40 wt.%, or at least 45 wt.% of naphtha and distillate. The hydrocarbon-containing feedstock may be a crude oil, or may be a topped crude oil.

[0059] The hydrocarbon-containing feedstock may also contain quantities of metals such as for example vanadium and nickel. The hydrocarbon-containing feedstock may contain at least 50 wppm vanadium up to 500 wppm vanadium and at least 20 wppm nickel up to 200 wppm nickel.

[0100] The hydrocarbon-containing feedstock may also contain quantities of sulfur and nitrogen. The hydrocarbon containing feedstock may contain at least 2 wt.% sulfur, or at least 3 wt.% sulfur up to 8 wt.% sulfur or up to 6 wt.% sulfur; and the hydrocarbon-containing feedstock may contain at least 0.25 wt.% nitrogen, or at least 0.4 wt.% nitrogen up to 2 wt% or up to 1 wt.% nitrogen.

[0101] The process of the present invention is particularly applicable to certain heavy petroleum and coal derived hydrocarbon-containing feedstocks. The hydrocarbon-containing feedstock may be a heavy or an extra-heavy crude oil containing significant quantities of residue or pitch; a topped heavy or topped extra-heavy crude oil containing significant quantities of residue or pitch; bitumen; hydrocarbons derived from tar sands; shale oil; crude oil atmospheric residues; crude oil vacuum residues; asphalts; and hydrocarbons derived from liquefying coal.

Hydrogen

[0102] The hydrogen that is mixed with the hydrocarbon-containing feedstock and the slurry catalyst in the process of the disclosure is derived from a hydrogen source. The hydrogen source may be hydrogen gas obtained from any conventional source or method for producing hydrogen gas.

[0103] A substantial portion of hydrogen provided to the horizontal reactor for mixing with the hydrocarbon-containing feedstock and the catalyst may be hydrogen that is recycled back into the reactor. Hydrogen may be separated from the reactor as a portion of the vapor product, and may be subsequently separated from condensable hydrocarbons in the vapor product by condensing the hydrocarbons from the vapor product in a high pressure separator and/or a low pressure separator after cooling the vapor product. Hydrogen may be separated from other components of the vapor product such as hydrogen sulfide by scrubbing the vapor product with a hydrogen sulfide scrubbing solvent such as an amine solvent. The separated hydrogen may be recycled back into the reactor.

Catalyst

[0104] The catalyst that is mixed with the hydrocarbon-containing feedstock and the hydrogen is one that is capable of activating molecular hydrogen and is referred to generally herein as a "hydrotreating" catalyst. The catalyst preferably promotes

hydrogenation of thermally cracked hydrocarbons to reduce coke byproduct formation to thereby improve yields of hydrocarbon products that may vaporize in the reactor and that are liquid at STP. The catalyst may also promote cracking when the catalyst is a dual function catalyst containing a portion suitable for inducing acid- or base- catalyzed cracking, for example an acidic or basic support, and a metal effective for activating molecular hydrogen to suppress the formation of coke. The catalyst may also promote hydrodesulfurization and hydrodenitrogenation activity.

[0105] Suitable catalysts for use in the present process include catalysts capable of activating molecular hydrogen including but not limited to metal oxides and metal sulfides. Exemplary catalysts for use in the present process include oxides and sulfides of nickel, cobalt, molybdenum, or tungsten,, and mixtures thereof. Metal oxide catalyst precursors may be sulfided to form metal sulfide catalysts for use in the process of the present invention according to conventional sulfiding processes or may be sulfided *in situ* in the reactor by contact with hydrogen sulfide produced in the process. The catalyst used in the process, for example, may be selected to include a molecular hydrogen activating metal selected from the group consisting of nickel oxide (NiO or Ni_2O_3), cobalt oxide (CoO, Co_2O_3, or Co_3O_4), molybdenum oxide (MoO_2 or MoO_3), tungsten oxide (W_2O, W_3O, W_2O_3, or W_2O_5), or mixtures thereof, such as nickel-molybdenum (Ni-Mo) oxide, or cobalt-molybdenum (CoMo) oxide, or nickel-tungsten (Ni-W) oxide. The catalyst used in the process may also be selected to include a molecular hydrogen activating metal that is selected from, and is preferably selected from, the group consisting of nickel sulfide (NiS, Ni_9S_8, or Ni_3S_2), cobalt sulfide (CoS_2, Co_3S_4, or Co_9S_8), molybdenum sulfide (MoS), molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), and mixtures thereof, including nickel-molybdenum sulfide, cobalt-molybdenum sulfide, nickel-tungsten sulfide, or cobalt-tungsten sulfide.

[0106] The catalyst used in the process may include a support such as an alumina or an alumina-silica support. Exemplary catalysts include mixed metal sulfides from Column 5, Column 6, and/or Column 8 of the Periodic Table such as Ni-Mo or Co-Mo or Ni-W, on an alumina or on an alumina-silica support. Column 5, 6 and/or column 8 metal compounds of the Periodic Table may be present in the supported catalyst in an amount of from 0.1 wt.% to 30 wt.%, more preferably from 0.5 wt.% to 15 wt.%. Molybdenum or tungsten compounds may be present in the supported catalyst in an amount of from 0.5

wt.% to 15 wt.%, more preferably from 1 wt.% to 10 wt.%. As described above, it is believed that the catalyst functions in the presence of the hydrogen gas to reduce coke byproduct formation by promoting the hydrogenation of coke precursors.

[0107] The catalyst may be a solid particulate substance having a particle size distribution with a relatively small mean or median particle size so the catalyst may form a mixture with the liquid hydrocarbon feed and liquid hydrocarbon-depleted residuum in the reactor, and in particular, may form a slurry with the liquid hydrocarbon feed and/or the liquid hydrocarbon-depleted residuum in the reactor as dispersed therein by the flow of hydrogen gas through the mixture of catalyst and liquid hydrocarbon feed and/or liquid hydrocarbon-depleted residuum. The catalyst may have a particle size distribution with a median or mean particle size of at least 500 nm, or at least 750 nm, or up to 1000 μm, or up to 750 μm; or up to 500 μm, or from 500 nm up to 1000μm. The solid particulate catalyst may be formed of a Column 6-8 metal compound of the Periodic Table dispersed on mineral oxide fines such as alumina fines or silica-alumina fines, where the alumina or silica-alumina fines have a particle size distribution wherein the mean particle size distribution of the fines is from 1 μm to 750 μm or at most 500 μm. The catalyst used in the process of the invention may be a solid particulate substance preferably having a particle size distribution with a mean or median particle size of up to 1000 μm, preferably having a pore size distribution with a mean pore diameter of from 50 angstroms to 500 angstroms, preferably having a porosity of at least 0.2 cm^3/g, and preferably having a BET surface area of at least 50 m^2/g.

[0108] The solid particulate catalyst is insoluble in the hydrocarbon-containing feed and in a hydrocarbon-depleted feed residuum formed by the process of the present invention. The use of a solid particulate catalyst which is insoluble in the hydrocarbon-containing feed and the hydrocarbon-depleted residuum is desirable in the present process, since the catalyst remains in the horizontal reactor rather than being removed with the vapor product, and is removed along with the residuum formed by the process.

Process for conversion of a hydrocarbon-containing feedstock

[0109] In the process provided herein, a hydrocarbon-containing feedstock as described above, a hydrotreating catalyst, and hydrogen are mixed at a total pressure of at least 2 MPa or at least 10 MPa in a horizontal reactor fitted with one or more vapor-only outlets,

where the hydrocarbon-containing feedstock, catalyst, and hydrogen form a mixture, the mixture comprising bubbles of hydrogen gas within the hydrocarbon feedstock. The hydrocarbon-containing feedstock, catalyst, and hydrogen are mixed at a temperature selected from 375°C to 550°C. The hydrocarbon-containing feedstock, catalyst and hydrogen are mixed by contact with each other in a mixing zone maintained at a temperature from 375°C to 550°C, and a total pressure of at least 2MPa or at least 10MPa, to provide a hydrocarbon-containing vapor product. The hydrogen gas may be at a hydrogen partial pressure of at least 2 MPa, or at least 10 MPa, or in a range from, for example, 2.0 MPa to 15.0 MPa. The hydrocarbon-containing vapor product comprises one or more hydrocarbon compounds that are liquid at STP, and is separated from the mixture in the mixing zone by removal from the reactor at the one or more vapor-only outlets.

[0110] In an embodiment of the process of the invention, as shown in Fig. 1, the mixing zone **1** is in a horizontal reactor **3**, where the conditions of the reactor **3** may be controlled to maintain the temperature and pressure in the mixing zone **1** at 375°C to 550°C and at a total pressure of at least 2 MPa or at least 10 MPa, and preferably a hydrogen partial pressure of at least 2 MPa or at least 10 MPa. The hydrocarbon-containing feedstock may be provided continuously or intermittently from a feed supply **2** to the mixing zone **1** in the horizontal reactor **3** through feed inlet **5**. The hydrocarbon-containing feedstock may be preheated to a temperature of from 100°C to 350°C by a heating element **4**, which may be a heat exchanger, prior to being fed to the mixing zone **1**. Hydrogen may be provided continuously or intermittently to the mixing zone **1** of the horizontal reactor **3** through hydrogen inlet line **7**, or, alternatively, may be mixed together with the hydrocarbon-containing feedstock, and optionally the catalyst, and provided to the mixing zone **1** through the feed inlet **5**. The hydrogen is introduced into the hydrocarbon-containing feedstock in the form of bubbles.

[0111] The solid particulate catalyst may be located in the mixing zone **1** in the reactor **3** or may be provided to the mixing zone **1** in the horizontal reactor **3** during the process of the present disclosure. The catalyst is provided to the mixing zone **1** during the process, or, if located in the mixing zone initially, may be blended as particles with the hydrocarbon-containing feed and hydrogen. The catalyst may be provided directly via a catalyst inlet to a mixing zone **1.** In some embodiments, as shown in Figs. 1, 5 and 6, the

catalyst may be provided to the mixing zone **1** together with the hydrocarbon-containing feedstock through feed inlet **5**, where the catalyst may be dispersed in the hydrocarbon-containing feedstock to form a catalyst-hydrocarbon containing feedstock slurry prior to feeding the mixture to the mixing zone **1** through the feed inlet **5**. The catalyst may be provided through a catalyst inlet **9** to a mixing tank **6** to which is provided hydrocarbon-containing feedstock **2**. The catalyst is then mixed with the hydrocarbon containing feedstock at mixing tank **6** which may be, for example, fitted with a mechanical stirring device, to enable the catalyst to be delivered to the mixing zone **1** through feed inlet **5** along with the hydrocarbon containing feedstock as a catalyst-hydrocarbon feedstock mixture.

[0112] The catalyst to be mixed with the hydrocarbon-containing feedstock and the hydrogen in the mixing zone **1** may be provided in an amount sufficient to stabilize the hydrocarbon-containing feedstock against coke formation. The catalyst may be provided for mixing with the hydrocarbon-containing feedstock and hydrogen in an amount of from 0.125 g to 250 g of catalyst per kg of hydrocarbon-containing feedstock. Alternatively, the catalyst may be provided for mixing with the hydrocarbon-containing feedstock and hydrogen in an amount of from 0.50 g to 100 g of catalyst per kg of hydrocarbons in the hydrocarbon-containing feedstock having an API Gravity of less than 20. The hydrocarbon-containing feedstock may be provided to the mixing zone **1** of the horizontal reactor **3** at a rate of from 0.05 m^3/hr of feed per m^3 reactor volume to 2 m^3/hr of feed per m^3 reactor volume.

[0113] Preferably, the mixture volume of the hydrocarbon-containing feedstock, the hydrocarbon-depleted feed residuum, and the catalyst(s) is maintained within the mixing zone within a selected range of the reactor volume by selecting 1) the rate at which the hydrocarbon-containing feedstock and catalyst are provided to the mixing zone **1**; and/or, optionally, 2) the rate at which a purge stream is removed from the reactor; and/or 3) the temperature and pressure within the mixing zone **1** and the horizontal reactor **3** to provide a selected rate of vapor product removal from the mixing zone **1** and the horizontal reactor **3**. The combined volume of the hydrocarbon-containing feedstock and the catalyst(s) initially provided to the mixing zone **1** at the start of the process define an initial mixture volume, and the amount of hydrocarbon-containing feedstock and the amount of the catalyst(s) initially provided to the mixing zone **1** may be selected to provide an initial

mixture volume of from 5% to 97% of the reactor volume, preferably from 30% to 75% of the reactor volume. The rate at which the hydrocarbon-containing feedstock is provided to the mixing zone **1** and/or the rate at which a purge stream is removed from the reactor and/or the rate at which vapor is removed from the reactor **3** may be selected to maintain the mixture volume of the hydrocarbon-containing feedstock, the hydrocarbon-depleted feed residuum, and the catalyst(s) at a level of at least 10%, or at least 25%, or within 90%, or within 70%, or within 50% of the initial mixture volume during the process.

[0114] Hydrogen may be provided to the mixing zone **1** of the horizontal reactor **3** at a rate sufficient to hydrogenate hydrocarbons cracked in the process. Hydrogen gas may be provided to the mixing zone **1** of the horizontal reactor **3** at a high gas velocity sufficient to enable substantially complete removal of hydrocarbon products from the reactor. The hydrogen may be provided to the mixing zone **1** at a linear gas velocity of from 0.03 to 6.0 meters per minute, or from 0.03 to 4.0 meters per minute, or from 0.03 to 3.0 meters per minute, or from 0.3 to 4.0 meters per minute, or from 0.3 feet to 3.0 meters per minute, or from 1.5 feet to 4.0 meters per minute, or from 1.5 meters to 3.0 meters per minute. The hydrogen gas may be introduced into the hydrocarbon-containing feedstock by a gas distribution system **8** configured to form gas bubbles in the hydrocarbon-containing feedstock liquid phase and laterally disposed along the length of the reactor **3.** In one or more preferred embodiments, the hydrogen gas may be introduced from a gas distribution system **8** to flow upwardly into the hydrocarbon-containing feedstock which enters the horizontal reactor at feed inlet **5** to thereby provide a flow of hydrogen bubbles into the liquid phase that is cross-current to the flow of the hydrocarbon-containing feedstock entering the reactor. The catalyst may be distributed vertically in the liquid phase by the upwardly directed flow of hydrogen and distributed horizontally in the liquid phase by the flow of the hydrocarbon-containing feedstock and catalyst entering the reactor at the feed inlet **5** and circulating from one end of the horizontal reactor to the other, to thereby provide a good distribution of the catalyst within the liquid phase. The gas distribution system **8** may be configured to introduce hydrogen gas bubbles into the hydrocarbon-containing feedstock at multiple locations **23** along the length of the reactor **3** as shown in Figs. 5 and 6. Typical bubble sizes will be in a range from about 0.5 mm to 75 mm , or preferably from 1 mm to 5 mm. Alternatively, in some embodiments, the hydrocarbon-containing feedstock, optionally mixed with the catalyst, may be introduced to the

horizontal reactor **3** from a feed inlet that is located on the upper surface of the reactor, and the hydrogen gas may be introduced from a gas distribution system **8** located on a lower surface of the horizontal reactor **3** and laterally disposed along the length thereof, to thereby create a flow of hydrogen gas bubbles that is countercurrent to the flow of the hydrocarbon-containing feedstock into the reactor.

[0115] As shown in Figs. 1, 5 and 6, initial hydrogen gas introduction to the reactor **3** may be made via hydrogen inlet line **7**. The hydrogen gas may be provided to the mixing zone **1** in a ratio relative to the hydrocarbon-containing feedstock provided to the mixing zone **1** (treat gas ratio) of from 800 Nm^3/m^3 to 5600 Nm^3/m^3 (5,000 SCFB to 35,000 SCFB), or from 960 Nm^3/m^3 to 4800 Nm^3/m^3 (6,000 SCFB to 30,000 SCFB), or from 1200 Nm^3/m^3 to 3200 Nm^3/m^3 (7,500 SCFB to 20,000 SCFB), or from 1600 Nm^3/m^3 to 2400 Nm^3/m^3 (10,000 SCFB to 15,000 SCFB). The hydrogen partial pressure in the reactor may be maintained in a pressure range of from at least 2.0 MPa to 15.0 MPa, or from 5.0 MPa to 14.0 MPa, or from 10.0 MPa to 13.5 MPa.

[0116] The temperature and pressure conditions in the mixing zone **1** are maintained so that heavy hydrocarbons in the hydrocarbon-containing feedstock may be cracked. The temperature in the mixing zone **1** is maintained from 375°C to 550°C. Preferably, the mixing zone **1** is maintained at a temperature of from 400°C to 550°C, or from 425°C to 525°C, or from 430°C to 500°C, or from 435°C to 475°C. Higher temperatures such as these may be preferred in the process of the present invention since 1) the rate of conversion of the hydrocarbon-containing feedstock to a hydrocarbon-containing product increases with temperature; and 2) the present process inhibits or prevents the formation of coke.

[0117] The horizontal reactor may be configured to have two or more stages, wherein the temperature and/or the hydrogen flow rate may be selected such that each stage of the reactor may have a different temperature range and/or a different hydrogen flow rate therein. Each stage may be in fluid connection with at least one other stage, and preferably is in fluid communication only with laterally adjacent stages. Vertical weirs can, for example, be used within the reactor to induce staging. One or more stages of the reactor may be a purge settling zone stage as described further herein. Each stage may

have separate vapor phase outlet therein so that vapor product from that stage may be removed from the reactor through the vapor phase outlet within that stage.

[0118] Temperature staging may be employed in the reactor such that the reactor comprises one or more reactor stages having different temperature ranges. For example, the reactor may comprise two or more stages disposed laterally along the length of the reactor, each having a different temperature range. The temperature ranges within the stages may, for example, progress from a lower temperature range in a stage proximal to the hydrocarbon feed inlet to a higher temperature range in a stage distal to the hydrocarbon feed inlet. Such temperature staging may be effective to optimize yields by, for example, protecting early-formed reactive vapor phase intermediates from further reaction or unselective side reactions, whilst providing higher temperature ranges for enhanced conversion of more refractory components at later stages of the conversion process. For example, which is no way intended to be limiting, a first stage may be maintained at a temperature from 375°C to 425°C, or from 400°C to 450°C, while a subsequent stage disposed laterally to a first stage and more distal to the hydrocarbon feed inlet may be maintained, for example, at a temperature from 400°C to 500°C, or from 425°C to 550°C, and so forth.

[0119] Hydrogen flow rate staging may be employed in the reactor such that the reactor comprises one or more reactor stages having different hydrogen flow rates. For example, the reactor may comprise two or more stages disposed laterally along the length of the reactor, each having a different hydrogen flow rate. The hydrogen flow rates (either linear velocity or volumetric) may decrease from a higher hydrogen flow rate in a stage proximal to the hydrocarbon feed inlet to a lower hydrogen flow rate in a stage distal to the hydrocarbon feed inlet. Such hydrogen flow rate staging may enhance gravity settling of larger coke particles, metals, and the catalyst in a purge settling zone stage, as described in further detail below.

[0120] Mixing the hydrocarbon-containing feedstock, the catalyst, and hydrogen in the mixing zone **1** at a temperature and a total pressure and a hydrogen partial pressure as described herein produces a vapor comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone **1**. The vapor may be comprised of hydrocarbons present initially in the hydrocarbon-containing feedstock that vaporize at the

temperature and pressure within the mixing zone **1** and hydrocarbons that are not present initially in the hydrocarbon-containing feedstock but are produced by cracking and hydrogenating hydrocarbons initially in the hydrocarbon-containing feedstock that were not vaporizable at the temperature and pressure within the mixing zone 1.

[0121] At least a portion of the vapor comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone 1 may be continuously or intermittently separated from the mixture of hydrocarbon-containing feedstock, hydrogen, and catalyst since the more volatile vapor physically separates from the hydrocarbon-containing feedstock, catalyst, and hydrogen bubble mixture. The vapor may also contain hydrogen gas, which also separates from the mixture, hydrogen sulfide gas, which forms as a result of cracking sulfur-containing heteroatoms, and small amounts of non-condensable hydrocarbons, for example a hydrocarbon gas formed of C1-C4 hydrocarbons.

[0122] Separation of the vapor from the mixture leaves a hydrocarbon-depleted feed residuum from which the hydrocarbons present in the vapor have been removed. The hydrocarbon-depleted feed residuum is comprised of hydrocarbons that are liquid at the temperature and pressure within the mixing zone 1. Solids such as metals freed from cracked hydrocarbons--a metal byproduct--and minor amounts of coke, generally 5% by weight or less relative to a liquid hydrocarbon product condensed from the total vapor product at STP, may also be left in the reactor with the liquid hydrocarbon-depleted feed residuum upon separation of the vapor product from the reactor. Little coke or proto-coke may be formed in the process of the present invention since the process of the present invention inhibits the generation of coke. At most 50 kg, or less than 30 kg, or at most 20 kg, or at most 10 kg, or at most 5 kg of hydrocarbons insoluble in toluene as measured by ASTM Method D4072 may be produced by the process of the present invention.

[0123] At least a portion of the liquid hydrocarbon-depleted feed residuum is retained in the mixing zone 1 while the vapor is separated from the mixing zone 1. The portion of the liquid hydrocarbon-depleted feed residuum retained in the mixing zone 1 may be subject to further cracking to produce more vapor that may be separated from the reactor **3** from which the liquid hydrocarbon-containing product may be produced by cooling. Hydrocarbon-containing feedstock, catalyst and hydrogen may be continuously or

intermittently provided to the mixing zone **1** at the rates described above and the hydrocarbon-depleted feed residuum retained in the mixing zone **1** to produce further vapor comprised of hydrocarbons that are vaporizable at the temperature and pressure within the mixing zone **1** for separation from the mixing zone **1** and the horizontal reactor **3**. The utilization of a horizontal reactor allows for variable residence times in the reactor, to thereby retain heavy unreacted components in the reacting environment of the liquid phase comprising hydrogen and catalyst for a longer period than lighter hydrocarbons. Moreover, the lateral transit of the hydrocarbon feedstock through the horizontal reactor may result in increased contact times of heavy unreacted components in the feed with the slurry catalyst and hydrogen bubbles therein relative to a comparable vertical reactor unit.

[0124] At least a portion of the vapor separated from the mixture of the hydrocarbon-containing feedstock, hydrogen, and catalyst may be continuously or intermittently separated from the mixing zone **1** while retaining the liquid hydrocarbon-depleted feed residuum, catalyst, and any fresh hydrocarbon-containing feedstock in the mixing zone **1**. At least a portion of the vapor separated from the mixing zone **1** may be continuously or intermittently separated from the reactor **3** through a reactor vapor product outlet **11**. The horizontal reactor **3** is preferably configured and operated so that substantially only vapors and gases may exit the reactor vapor product outlet **11**, where the vapor product exiting the reactor **3** comprises at most 5 wt.%, or at most 3 wt.%, or at most 1 wt.%, or at most 0.5 wt.%, or at most 0.1 wt.%, or at most 0.01 wt.%, or at most 0.001 wt.% solids and liquids at the temperature and pressure at which the vapor product exits the horizontal reactor **3**.

[0125] Referring now to Fig. 1, in the present process, the hydrocarbons in the hydrocarbon-containing feed are contacted and mixed with the catalyst and hydrogen in the mixing zone **1** of the reactor for only as long as is necessary to be vaporized and separated from the mixture, and are retained in the reactor **3** only as long as necessary to be vaporized and exit the reactor product outlet **11**. Low molecular weight hydrocarbons having a low boiling point may be vaporized almost immediately upon being introduced into the mixing zone **1** when the mixing zone **1** is maintained at a temperature of 400°C to 550°C and a total pressure of at least 2.0 MPa, for example from 10.0 to 25.0 MPa. The use of a high hydrogen volumetric flow rate of about 800 Nm^3(hydrogen)/m^3(feedstock) to 4000 Nm^3(hydrogen)/m^3(feedstock), further assists in vaporizing low molecular weight

hydrocarbons having a low boiling point. These hydrocarbons may be separated rapidly from the reactor **3**. Asphaltenes, present in the hydrocarbon feedstock, can undesirably precipitate during the hydroprocessing reaction, thereby leading to increased solids production during processing. However, high molecular weight hydrocarbons such as aromatics and resins tend to maintain the asphaltenes suspended in the hydrocarbon-containing feedstock. Thus, the rapid separation of low molecular weight hydrocarbons from the horizontal reactor is advantageous, since as a result, the liquid phase remaining in the reactor will be enriched in higher molecular weight hydrocarbons such as aromatics and resins, to thereby reduce the potential for asphaltene precipitation within the liquid phase in the reactor. High molecular weight hydrocarbons having a high boiling point, for example hydrocarbons having a boiling point greater than 538°C at 0.101 MPa, may remain in the mixing zone **1** until they are cracked into hydrocarbons having a boiling point low enough to be vaporized at the temperature and pressure in the mixing zone **1** and to exit the reactor **3**. The hydrocarbons of the hydrocarbon-containing feed, therefore, are contacted and mixed with the catalyst and hydrogen in the mixing zone **1** of the reactor **3** for a variable time period, depending on the boiling point of the hydrocarbons under the conditions in the mixing zone **1** and the lateral dimension of reactor **3**.

[0126] The rate of the process of producing the vapor product from the hydrocarbon-containing feedstock may be adjusted by selection of the temperature and/or pressure in the reactor **3**, and particularly in the mixing zone **1**, within the temperature range of 375°C-550°C and within a total pressure range of 2.0 MPa to 25.0 MPa. Increasing the temperature and/or decreasing the pressure in the mixing zone **1** permits the hydrocarbon-containing feedstock to be provided to the reactor **3** at an increased rate and the vapor product to be removed from the reactor **3** at an increased rate since the hydrocarbons in the hydrocarbon-containing feedstock may experience a decreased residence time in the reactor **3** due to higher cracking activity and/or faster vapor removal. Conversely, decreasing the temperature and/or increasing the pressure in the mixing zone **1** may reduce the rate at which the hydrocarbon-containing feedstock may be provided to the reactor **3** and the vapor product may be removed from the reactor **3** since the hydrocarbons in the hydrocarbon-containing feedstock may experience an increased residence time in the reactor **3** due to lower cracking activity and/or slower vapor removal.

[0127] At least a portion of the vapor separated from the mixing zone **1** and separated from the reactor **3** may be condensed and collected apart from the reactor to produce the liquid hydrocarbon-containing product. Referring now to Fig. 2, the portion of the vapor separated from the reactor **3** may be provided to a condenser **13** wherein at least a portion of the vapor separated from the reactor **3** may be condensed to produce the hydrocarbon-containing product that is comprised of hydrocarbons that are a liquid at STP. A portion of the vapor separated from the reactor **3** may be passed through a heat exchanger **15** to cool the vapor prior to providing the vapor to the condenser **13**.

[0128] As shown in Fig. 2, condensation of the liquid hydrocarbon-containing product from the vapor separated from the reactor via the reactor product outlet **11** may also produce a non-condensable gas that may be comprised of hydrocarbons having a carbon number from 1 to 4, hydrogen, and hydrogen sulfide. The condensed hydrocarbon-containing liquid product may be separated from the non-condensable gas through a condenser liquid product outlet **17** of condenser **13** and stored in a product receiver **18**, and the non-condensable gas may be separated from the condenser **13** through a non-condensable gas outlet **19**. The non-condensable gas may be passed through an amine or caustic scrubber **20** to separate hydrogen sulfide from the gas, and hydrogen-sulfide depleted gas may recovered through a gas product outlet **22**. The hydrogen sulfide-depleted gas, comprised of hydrogen and small quantities of C1-C4 hydrocarbons, may be recycled into the reactor via the hydrogen inlet line.

[0129] As provided in Fig. 3, alternatively, the portion of the vapor separated from the reactor via the reactor product outlet **11** may be provided to a high pressure separator **12** to separate a liquid hydrocarbon-containing product from gases not condensable at the temperature and pressure within the high pressure separator **12**, and the liquid hydrocarbon-containing product collected from the high pressure separator may be provided through line **16** to a low pressure separator **14** operated at a pressure less than the high pressure separator **12** to separate the liquid hydrocarbon-containing product from gases that are not condensable at the temperature and pressure at which the low pressure separator **14** is operated. The vapor/gas exiting the reactor through the reactor product outlet **11** may be cooled prior to being provided to the high pressure separator **12** by passing the vapor/gas through heat exchanger **15**. The condensed hydrocarbon-containing liquid product may be separated from the non-condensable gas in the low pressure

separator through a low pressure separator liquid product outlet **10** and stored in a product receiver **18**. The non-condensable gas may be separated from the high pressure separator **12** through a high pressure non-condensable gas outlet **24** and from the low pressure separator **14** through a low pressure non-condensable gas outlet **26**. The non-condensable gas streams may be combined in line **28** and passed through an amine or caustic scrubber **20** to remove hydrogen sulfide and recovered through a gas product outlet **22**. The resulting non-condensable gas, comprised of hydrogen and small quantities of C1-C4 hydrocarbons, may be recycled into the reactor via the hydrogen inlet line.

[0130] Alternatively, the vapor separated from the mixing zone **1** and from the reactor **3** may be further hydroprocessed without condensing the hydrocarbon-containing product. For example, the vapor separated from the reactor may be hydrotreated to reduce sulfur, nitrogen, and olefins in the hydrocarbon-containing product by passing the vapor from the reactor **3** to a hydroprocessing reactor, where the vapor may be contacted with a conventional hydroprocessing catalyst and hydrogen at a temperature of from 260°C to 425°C and a total pressure of from 3.4 MPa to 27.5 MPa.

[0131] Vapor product may be removed from the horizontal reactor **3** from more than one separate reactor vapor product outlets **11** located at different positions along length of the upper surface of the horizontal reactor as shown in Fig. 6. The one or more separate reactor vapor outlets allow withdrawal of vapor products having different compositions from different outlet locations along the length of the horizontal reactor, for routing to various post-processing steps. For instance, an olefinic-rich vapor product may be removed from a first vapor outlet most proximal to the feed inlet **5** and routed to a recovery or hydrogenation unit, while vapor products from additional reactor vapor outlet streams may proceed to other suitable post-processing steps such as hydrodesulfurization, hydrodenitrogenation, separation of fractions, and the like.

[0132] As shown in Figs. 1 and 4, a portion of the liquid hydrocarbon-depleted feed residuum, optional coke product, optional metal byproduct, and catalyst(s) may be separated from the mixing zone as a purge or bleed stream outlet **25** to remove solids including metals and hydrocarbonaceous solids including coke. Fig. 4 provides a simplified overview of an embodiment of the present process. As shown in Figs. 1 and 4, the reactor **3** may include a purge/bleed stream outlet **25** for removal of a stream of liquid

hydrocarbon-depleted feed residuum, optional metals byproduct, and catalyst(s) from the mixing zone **1** of the horizontal reactor **3.** The liquid hydrocarbon-depleted feed residuum may possess a high concentration of unreactive high conversion refractory products (i.e., unreactive end-of-conversion hydrocarbons) that have failed to undergo cracking to a product vaporizable at the temperature and pressure within the mixing zone. The ability to remove high refractory liquid products from the mixing zone **3** via bleed stream **25** of the reactor along with coke rather than purge a fully backmixed mixture, including a substantial portion of unreacted feed, provides an additional economic advantage by providing reduced losses of reactive hydrocarbon feed components to the purge stream. The bleed stream outlet **25** may be operatively connected to the mixing zone **1** of the reactor **3**.

[0133] A portion of the liquid hydrocarbon-depleted feed residuum, coke byproduct, metals byproduct, and the catalyst(s) may be removed together from the mixing zone **1** and the reactor **3** through the bleed stream outlet **25** while the process is proceeding to avoid accumulation of coke byproduct and spent catalyst in the reactor. Solids and the catalyst(s) may be separated from a liquid portion of the hydrocarbon-depleted feed residuum in a solid-liquid separator **30** as shown in Fig. 6. The solid-liquid separator **30** may be a filter or a centrifuge. The liquid portion of the hydrocarbon-depleted feed residuum may be recycled back into a portion of the mixing zone **1** distal from the hydrocarbon feedstock inlet **5** via a recycle inlet (not shown) for further processing or may be combined with the hydrocarbon-containing feed and recycled through the mixing zone **1** through the feed inlet **5**.

[0134] As shown in Figs. 4 - 6, the reactor **3** may also contain a purge settling zone **21** in fluid communication with the mixing zone **1** of reactor **3.** The purge settling zone is positioned downstream of the hydrocarbon feedstock inlet **5**, typically at the horizontal end of the reactor opposite to the hydrocarbon feedstock inlet **5**. The purge settling zone **21** allows for concentration of byproduct coke, byproduct metals, and catalyst solids relative to their content in mixing zone **1**.

[0135] The purge settling zone **21** in fluid connection with mixing zone **1** may comprise an overflow weir. The purge settling zone **21** may further comprise a reduced flow of hydrogen gas into the liquid phase contained therein, relative to the flow of hydrogen gas

into the hydrocarbon feedstock-catalyst slurry contained in mixing zone **1,** to thereby allow gravity setting of larger coke particles, metals, and catalyst in the purge zone, where the hydrogen gas flow rate to the purge settling zone may be less than 0.25 ft/min (50 m/hr) or 0.1 ft/min (20 m/hr), or 0.05 ft/min (10 m/hr). The provision of a reduced flow of hydrogen gas in the purge settling zone **21** (i.e., reduced hydrogen gas injection) relative to the mixing zone **1** may be effective to maintain suppression of coke formation while also enabling gravity settling of solids. This feature may be due at least in part to the staging of the liquid phase composition within mixing zone **1** of the horizontal reactor **3** as it circulates towards the purge settling zone **21**. That is to say, separation of the vapor product from the mixture of hydrocarbon-containing feedstock, hydrogen, and catalyst leaves a hydrocarbon-depleted feed residuum from which the hydrocarbons present in the vapor have been removed. Since the hydrocarbon-depleted feed residuum is comprised of hydrocarbons that are liquid at the temperature and pressure within the mixing zone **1,** i.e., is mostly refractory, the residuum will possess low hydrogen consumption rates such that reduced hydrogen gas sparging in the settling zone will still be effective to suppress coke formation.

[0136] Additional solids-based separation steps may be employed to fluidize the catalyst and smaller coke particles away from the large coke particles collected in the purge settling zone **21**. Suitable solids-based separations include filtration, optionally using sintered metal filters, ceramic filters membrane-based processes, or use of hydrocyclones, centrifuges, or holding tanks for gravity separation. Thus, the instant process is capable of not only providing a separation of catalyst particles from coke byproduct, but is also effective to concentrate solids relative to unconverted liquid product.

[0137] The instant process is not constrained by dimensions of the horizontal reactor, with the exception that the reactor is configured to have a length that is greater than its height. Suitable individual reactor units may have a length of from 30 meters to 95 meters, or from 35 meters to 95 meters, or from 45 meters to 95 meters, or from 35 meters to 75 meters, or from 45 meters to 60 meters. The horizontal reactor may possess a diameter of from 3 meters to 7.5 meters, or from 3.5 meters to 7.0 meters, or from 4.5 meters to 7.0 meters, or from 4.5 meters to 6.0 meters. A horizontal reactor for use in the instant process may possess a length-to-diameter ratio of in a range from 30-to-1 to 10-to-1, or from 20-to-1 to 10-to-1.

[0138] One or more horizontal reactors may also be fluidly coupled to one another, to be limited only by available space constraints. That is to say, a first horizontal reactor may by fluidly coupled to a second horizontal reactor in an end-to-end configuration, or a side-by-side configuration, or in a stacked configuration. The horizontal reactors may be fluidly coupled in series such that the hydrocarbon feed inlet of a horizontal reactor may receive liquid hydrocarbon-depleted residuum exiting a preceding horizontal reactor as the hydrocarbon feed therein. The process of the present invention produces, in part, a hydrocarbon-containing product that is a liquid at STP. The hydrocarbon-containing product may contain less than 3 wt.%, or at most 2 wt.%, or at most 1 wt.%, or at most 0.5 wt.% of hydrocarbons having a boiling point of greater than 538°C as determined in accordance with ASTM Method D5307. Furthermore, the hydrocarbon-containing product may contain at least 80%, or at least 85%, or at least 90% of the atomic carbon present in the hydrocarbon-containing feedstock. Therefore, when the process of the present invention is utilized, most of the hydrocarbons in the hydrocarbon-containing feedstock may be recovered in the hydrocarbon-containing product that is liquid at STP, and little of the hydrocarbons in the hydrocarbon-containing feedstock are converted to coke or gas.

[0139] The hydrocarbon-containing product may contain VGO hydrocarbons, distillate hydrocarbons, and naphtha hydrocarbons. The hydrocarbon-containing product may contain, per gram, at least 0.05 grams, or at least 0.1 grams of hydrocarbons having a boiling point from the initial boiling point of the hydrocarbon-containing product up to 204°C (400°F). The hydrocarbon-containing product may also contain, per gram, at least 0.1 grams, or at least 0.15 grams of hydrocarbons having a boiling point of from 204°C (400°F) up to 260°C (500°F). The hydrocarbon-containing product may also contain, per gram, at least 0.25 grams, or at least 0.3 grams, or at least 0.35 grams of hydrocarbons having a boiling point of from 260°C (500°F) up to 343°C (650°F). The hydrocarbon-containing product may also contain, per gram, at least 0.3 grams, or at least 0.35 grams, or at least 0.4, or at least 0.45 grams of hydrocarbons having a boiling point of from 343°C (500°F) up to 510°C (950°F). The relative amounts of hydrocarbons within each boiling range and the boiling range distribution of the hydrocarbons may be determined in accordance with ASTM Method D5307.

[0140] The hydrocarbon-containing product produced by the process of the present invention may contain significant amounts of sulfur. The hydrocarbon-containing product may contain, per gram, at least 0.0005 gram of sulfur or at least 0.001 gram of sulfur. The sulfur content of the hydrocarbon-containing product may be determined in accordance with ASTM Method D4294. The sulfur-containing hydrocarbon compounds in the hydrocarbon-containing product may be primarily benzothiophenic compounds. In the hydrocarbon-containing product, at least 70 wt.% of the sulfur may be contained benzothiophenic compounds. At least 75 wt.% or at least 80 wt.%, or at least 85 wt.% of the sulfur in the hydrocarbon-containing product may be contained in benzothiophenic compounds. The amount of sulfur in benzothiophenic compounds in the hydrocarbon-containing product relative to the amount of sulfur in all sulfur containing compounds in the hydrocarbon-containing product may be determined by sulfur chemiluminscence two dimensional gas chromatography (GCxGC-SCD).

[0141] The hydrocarbon-containing product produced by the process of the present invention may contain, per gram, at least 0.0005 gram or at least 0.001 gram of nitrogen as determined in accordance with ASTM Method D5762. The hydrocarbon-containing product may have a relatively low ratio of basic nitrogen compounds to other nitrogen containing compounds therein. The nitrogen may be contained in hydrocarbon compounds, where the nitrogen containing hydrocarbon compounds in the hydrocarbon-containing product may be primarily carbazolic compounds and acridinic compounds. In the hydrocarbon-containing product at least 70 wt.%, or at least 75 wt.%, or at least 80 wt.%, or at least 85 wt.% of the nitrogen in the hydrocarbon-containing product may be contained in carbazolic compounds and acridinic compounds. The amount of nitrogen in carbazolic and acridinic compounds relative to the amount of nitrogen in all nitrogen containing compounds in the hydrocarbon-containing product may be determined by nitrogen chemiluminscence two dimensional gas chromatography (GCxGC-NCD).

[0142] The hydrocarbon-containing product produced by the process of the present invention may contain significant quantities of aromatic hydrocarbon compounds. The hydrocarbon-containing product may contain, per gram, at least 0.3 gram, or at least 0.35 gram, or at least 0.4 gram, or at least 0.45 gram, or at least 0.5 gram of aromatic hydrocarbon compounds.

[0143] The hydrocarbon-containing product of the process of the present invention may contain relatively few polyaromatic hydrocarbon compounds containing two or more aromatic ring structures (e.g. naphthalene, benzothiophene, bi-phenyl, quinoline, anthracene, phenanthrene, di-benzothiophene) relative to mono-aromatic hydrocarbon compounds (e.g. benzene, toluene, pyridine). The mono-aromatic hydrocarbon compounds in the hydrocarbon-containing product may be present in the hydrocarbon-containing product in a weight ratio relative to the polyaromatic hydrocarbon compounds (containing two or more aromatic ring structures) of at least 1.5 : 1.0, or at least 2.0 : 1.0, or at least 2.5 : 1.0. The relative amounts of mono-aromatic and polyaromatic compounds in the hydrocarbon-containing product may be determined by flame ionization detection-two dimensional gas chromatography (GCxGC-FID).

[0144] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

[0145] EXAMPLES

[0146] Example 1

[0147] Heavy oil conversion studies were conducted at two different hydrogen volumetric flow rates to determine the effect of the rate of stripping of vapor product on coke formation. Two heavy oil conversion studies were conducted in a 1-Liter 316 stainless steel stirred reactor from Autoclave Engineers. A 4-blade downward thrusting pitch blade impeller was employed at 1200 rpm. Bitumen feed was supplied from a heated reservoir on level control using a piston pump with graphite filled PTFE seals. A ^{137}Cs gamma ray level detector was used to assess liquid level at 50% of the reactor volume. H_2 was supplied and metered as feed from a bottom port. Only vapor products were removed from the reactor, and routed to a high pressure condenser operated at greater than 10.0 MPa for condensation of liquid products and venting of the excess flow of hydrogen and other noncondensible gases. In this manner, an effective reaction rate could be assessed as the feed rate required to maintain level for the pseudo-steady state observed before the reactor filled with coke and metals from hydrotreating the feed.

[0148] In a first study, a 5 wt% slurry of a nickel-molybdenum on alumina hydrotreating catalyst (2 – 25 micron particle size distribution with a mean of 10 microns) was employed as catalyst at 430°C and 13.2 MPa total pressure. Hydrogen was supplied at a 900 standard liter per hour volumetric flowrate. It was found that a pseudo-steady state feed rate of about 125 g/hr could be maintained at 100 hours after the start of the run.

[0149] In a second study, a 5 wt% slurry of a nickel-molybdenum on alumina hydrotreating catalyst (2 – 25 micron particle size distribution with a mean of 10 microns) was employed as catalyst at 430°C and 13.2 MPa total pressure. Hydrogen was supplied at a 600 standard liter per hour volumetric flowrate. It was found that the pseudo-steady state feed rate was reduced to about 100 g/hr at 100 hours after the start of the run. Coke formation was assessed at the end of the run as about 1.0 wt.% based on the feed.

[0150] These studies showed the importance of high volumetric flow rate of hydrogen to the reactor to provide stripping and off-take of product from the reactor, thereby allowing a higher rate of conversion of the feedstock.

[0151] Example 2

[0152] The effect of hydrogen partial pressure in vapor out heavy oil conversion relative to the production of coke was determined at 3 different hydrogen partial pressures. A bitumen feed was hydrotreated in accordance with conditions as set forth in the second study of Example 1 except that in a first run the hydrogen partial pressure was maintained at 10.0 MPa, in a second run the hydrogen partial pressure was maintained at 7.6 MPa, and in a third run the hydrogen partial pressure was maintained at 6.5 MPa. The coke formation was then measured for each run. Coke formation in the first run (hydrogen partial pressure 10.0 MPa) was found to be 1.05 wt.% coke (relative to feed), which was substantially similar to the 1.0 wt.% coke (relative to feed) formation at 13.2 MPa hydrogen partial pressure observed in the second study of Example 1. Coke formation increased significantly, however, at lower hydrogen partial pressures, where coke formation in the second run (hydrogen partial pressure of 7.6 MPa) was found to be 2.8 wt.% (relative to feed) and in the third run (hydrogen partial pressure of 6.5 MPa) was found to be 3.6 wt.% (relative to feed). These results show the importance of maintaining a relatively high hydrogen partial pressure in the hydroconversion reaction to suppress coke formation.

[0153] Example 3

[0154] The effect of high linear gas velocity on liquid entrainment in vapor product was determined. A glass bubble column was operated with deionized water as solvent, and charged with 2 wt% of the NiMo on alumina catalyst used in the above experiments. Nitrogen gas was sparged for mixing at ambient pressure. Nitrogen gas flowrate was varied, and samples were remove from 3 cm below the top liquid level of the bubble column to assess slurry concentrations. A minimum of 0.07 ft/min (14 m/hr) linear gas velocity was required to mix catalyst uniformly from bottom to top of the bubble column. As gas flowrate increased above 0.5 ft/min (100 m/hr), entrainment of catalyst particle with liquid spray became evident at the top of the reactor.

[0155] These results show a minimum liquid gas velocity to suspend catalyst was 0.07 ft/min (14 m/hr), and entrainment of liquid and catalyst out of the reactor at higher gas velocity occurred above 0.5 ft/min (100 m/h).

[0156] The present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. While systems and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from a to b," or, equivalently, "from a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Whenever a numerical range having a specific lower limit only, a specific upper limit only, or a specific upper limit and a specific lower limit is disclosed, the range also includes any numerical value "about" the specified lower limit and/or the specified upper limit. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. Moreover, the indefinite articles "a" or

"an", as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

CLAIMS

1. A process for conversion of a hydrocarbon feedstock, the process comprising:

introducing a hydrocarbon feedstock having an API Gravity of less than 20, a solid particulate hydrotreating catalyst capable of activating molecular hydrogen, and hydrogen gas into a horizontal reactor having a length that is greater than its height, wherein the reactor is fitted with one or more separate vapor-only outlets and has one or more stages, where the hydrogen gas is introduced into the horizontal reactor as bubbles to a mixture of the hydrocarbon feedstock and the solid hydrotreating catalyst;

contacting the hydrocarbon feedstock- solid hydrotreating catalyst mixture and the bubbles of hydrogen gas at a temperature of from 375°C to 550°C and a total pressure of at least 2 MPa to produce a vapor product and a liquid hydrocarbon-depleted residuum, optionally with formation of a coke byproduct and a metals byproduct;

removing the vapor product from the horizontal reactor through the one or more separate vapor-only outlet locations downstream from a hydrocarbon feedstock inlet along the length of the horizontal reactor; and

removing the liquid hydrocarbon-depleted residuum, catalyst solids, optional metals byproduct, and optional coke byproduct from the reactor in one or more purge zones positioned downstream from the hydrocarbon feedstock inlet along the length of the horizontal reactor.

2. The process of claim 1, wherein the hydrocarbon feedstock and the solid hydrotreating catalyst are pre-mixed to form a slurry prior to the introducing step.

3. The process of claim 1, wherein the hydrocarbon feedstock and the hydrotreating catalyst are introduced to flow laterally along the length of the reactor, and the hydrogen gas is introduced to flow upwardly to thereby create a flow of the hydrocarbon feedstock and hydrocracking catalyst that is cross-current to the upward flow of the hydrogen gas.

4. The process of claim 1, wherein the one or more separate vapor-only outlet locations are positioned along an upper surface of the reactor.

5. The process of claim 1, wherein the vapor product is removed from the one or more vapor-only outlet locations at a linear velocity of less than 15 feet per minute.

6. The process of claim 1, further comprising recirculating at least a portion of the hydrogen gas separated from the vapor product to the mixture of liquid hydrocarbon feedstock, catalyst, and optionally liquid hydrocarbon-depleted residuum in the reactor.

7. The process of claim 1, wherein the one or more purge zones are positioned at the lateral end of the horizontal reactor distal to the hydrocarbon feedstock inlet.

8. The process of claim 1, wherein the contacting step produces a coke byproduct, and the purge zone comprises a weir, whereby the hydrogen flow in the purge zone is less than the hydrogen flow in the introducing step to thereby allow gravity settling of the coke byproduct catalyst solids, and optionally metals byproduct.

9. The process of claim 1, wherein the hydrocarbon feedstock, catalyst, and hydrogen are contacted at a temperature in a range of 400 to 550°C.

10. The process of claim 1, wherein the hydrotreating catalyst is selected from nickel sulfide, cobalt sulfide, molybdenum sulfide, tungsten sulfide, and mixtures thereof, on an alumina or alumina-silica support.

11. The process of claim 1, wherein the hydrogen gas is at a hydrogen partial pressure ranging from 10.0 to 15.0 MPa.

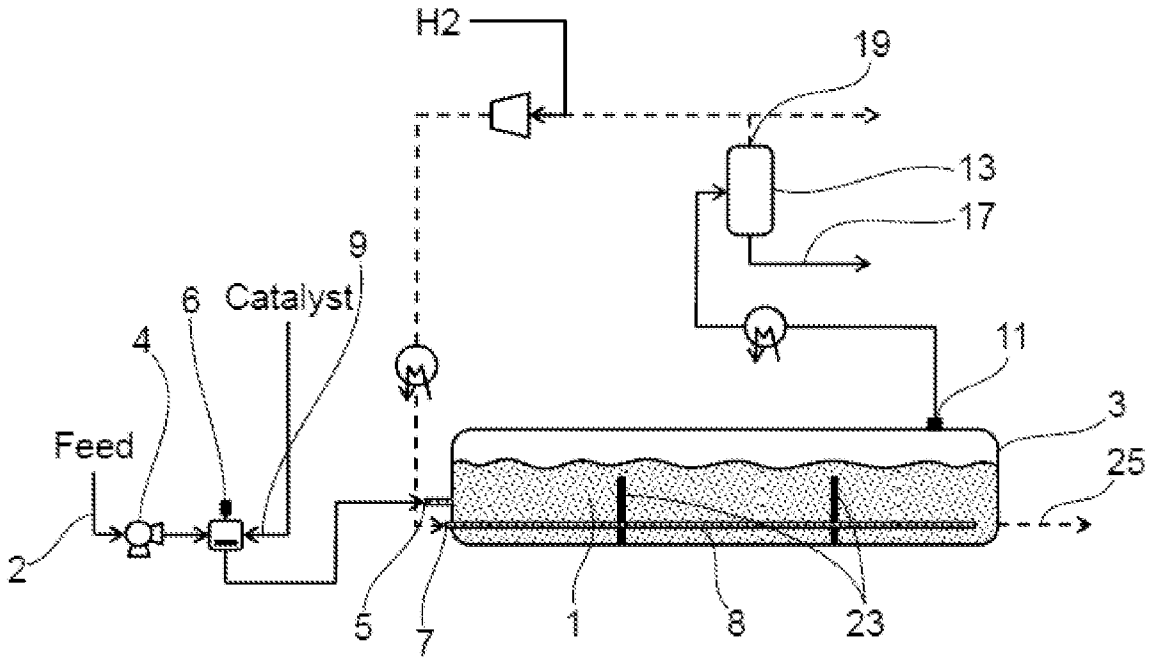

H2
19
13
17
9
6
Catalyst
4
11
3
Feed
25
2
5
7
1
8
23

FIG. 1

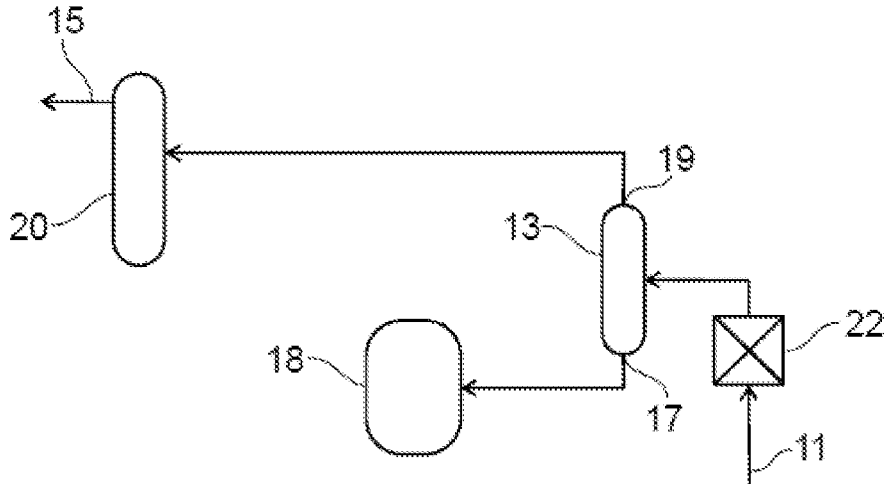

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FIG. 2

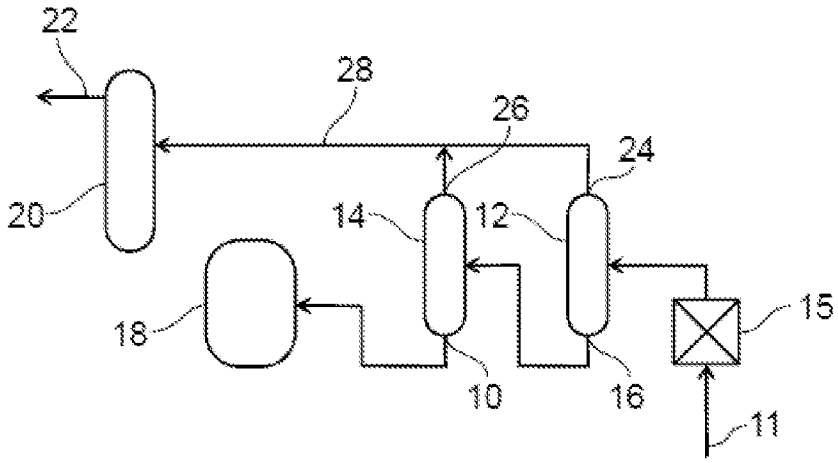
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FIG. 3

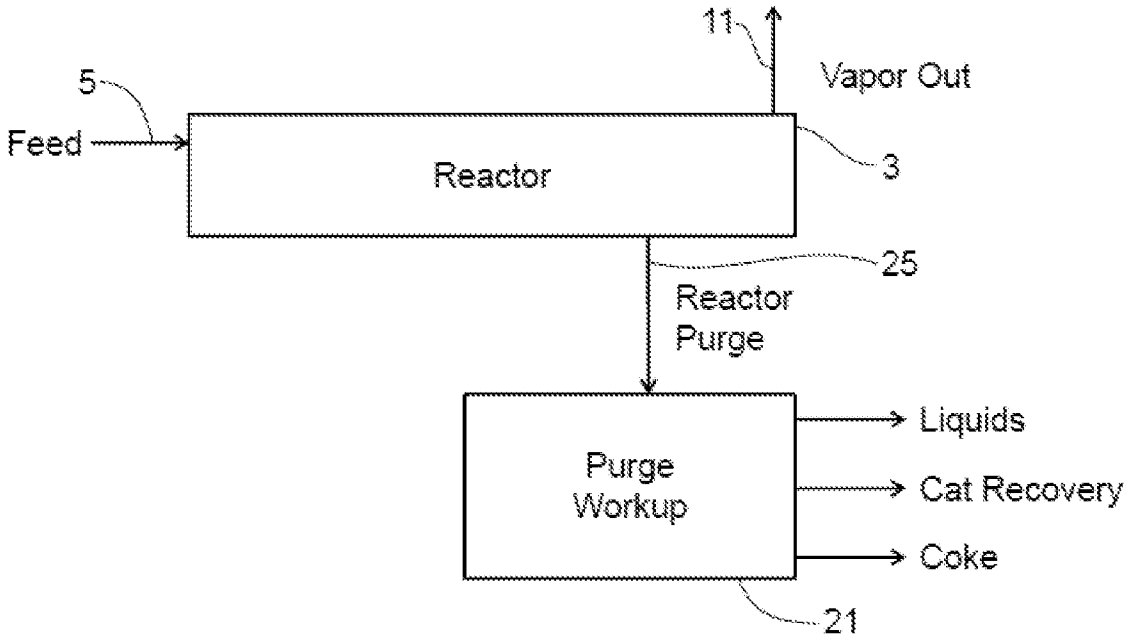
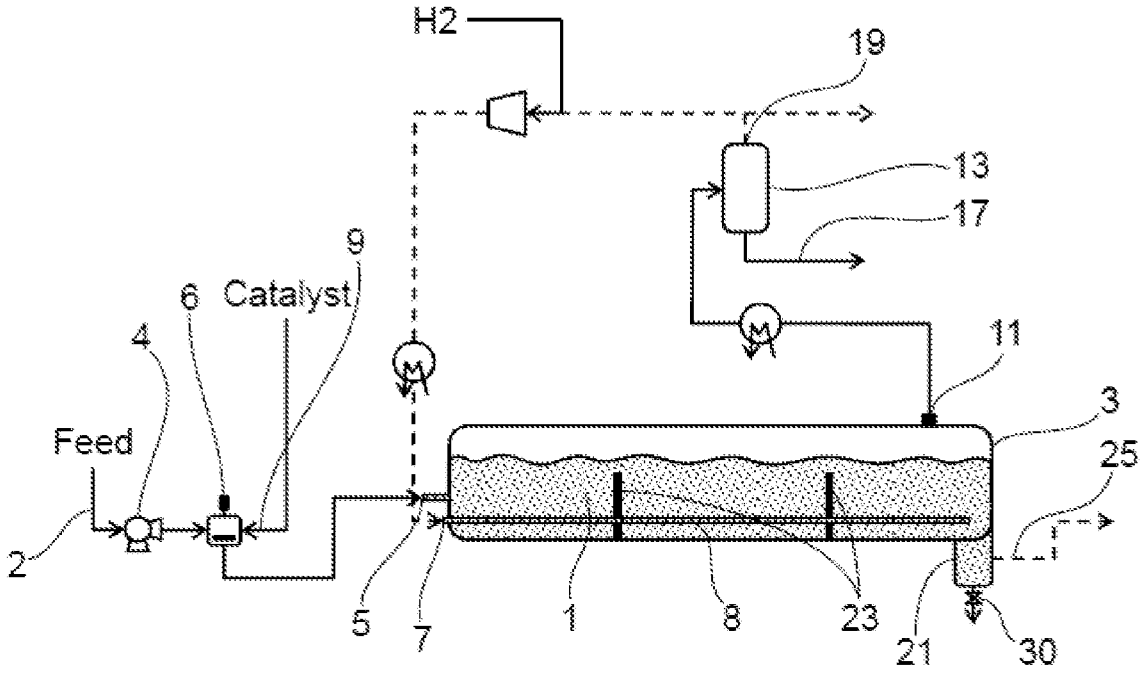

11
Vapor Out
5
Feed
Reactor
3
25
Reactor
Purge
Liquids
Purge
Workup
Cat Recovery
Coke
21

FIG. 4


H2
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Catalyst
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Feed
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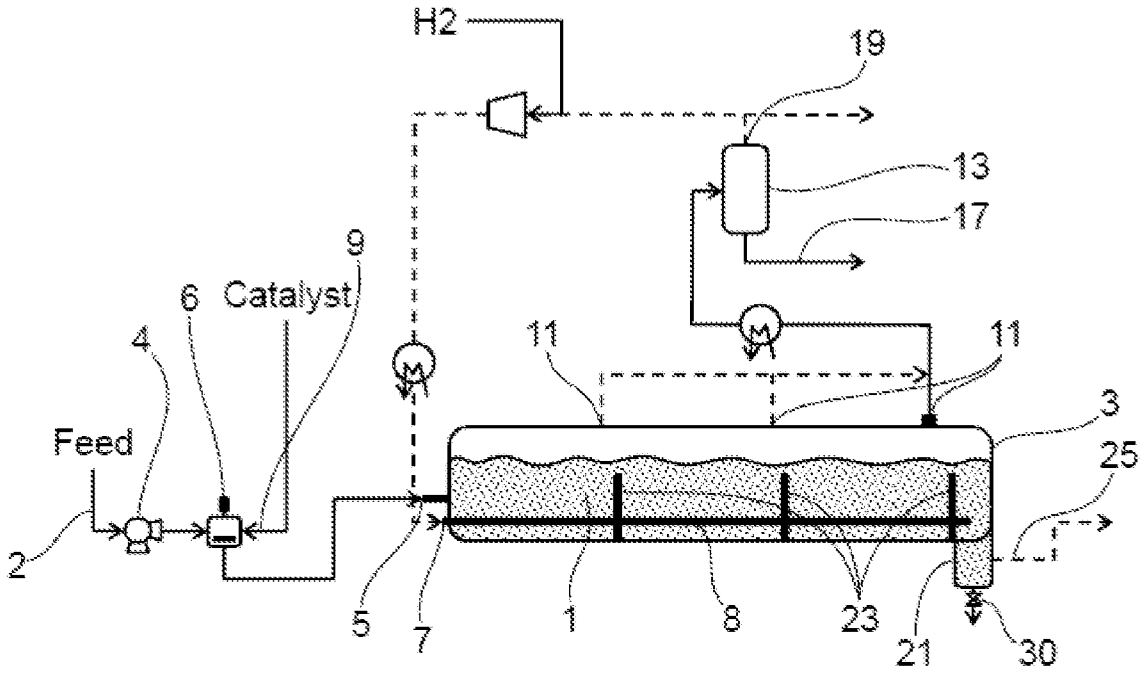
FIG. 5


H2
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Catalyst
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Feed
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21
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FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/067132

A. CLASSIFICATION OF SUBJECT MATTER

C10G 11/00(2006.01)i, C10G 31/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G 11/00; C10G 37/00; B01J 8/08; C10G 57/00; C10G 69/04; C10G 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: horizontal bubble reactor, hydrogen gas, hydrotreating catalyst, crack

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013-0062250 A1 (GAO, YONGCAN et al.) 14 March 2013 See claim 54.	1-11
A	US 4180453 A (FRANCK, JEAN-PIERRE et al.) 25 December 1979 See claim 1.	1-11
A	KR 10-0644987 B1 (CHINA PETROLEUM & CHEMICAL CORPORATION) 13 November 2006 See claim 1.	1-11
A	US 2011-0000818 A1 (XU, YOUHAO et al.) 6 January 2011 See claim 1.	1-11
A	US 2003-0124034 A1 (WU, XUEFENG et al.) 3 July 2003 See claim 1.	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 April 2016 (12.04.2016)	**14 April 2016 (14.04.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
KANG, Min Jeong
Telephone No. +82-42-481-8131

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/067132

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