



- (51) International Patent Classification:
C10G 65/10 (2006.01) C10G 47/26 (2006.01)
- (21) International Application Number:
PCT/US2013/070711
- (22) International Filing Date:
19 November 2013 (19.11.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13/777,508 26 February 2013 (26.02.2013) US
- (71) Applicant: CHEVRON U.S.A. INC. [US/US]; 6001 Bollinger Canyon Road, San Ramon, CA 94583 (US).
- (72) Inventors: KOU, Bo; 6001 Bollinger Canyon Road, San Ramon, CA 94583 (US). CHABOT, Julie; 6001 Bollinger Canyon Road, San Ramon, CA 94583 (US). REYNOLDS, Bruce, Edward; 6001 Bollinger Canyon Road, San Ramon, CA 94583 (US).
- (74) Agents: FLAHERTY, Terrence, M. et al.; Chevron Corporation, Law Department, P.O. Box 6006, San Ramon, CA 94583-0806 (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, LT, 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, 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, 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).

[Continued on next page]

(54) Title: RECONFIGURATION OF RECIRCULATION STREAM IN UPGRADING HEAVY OIL

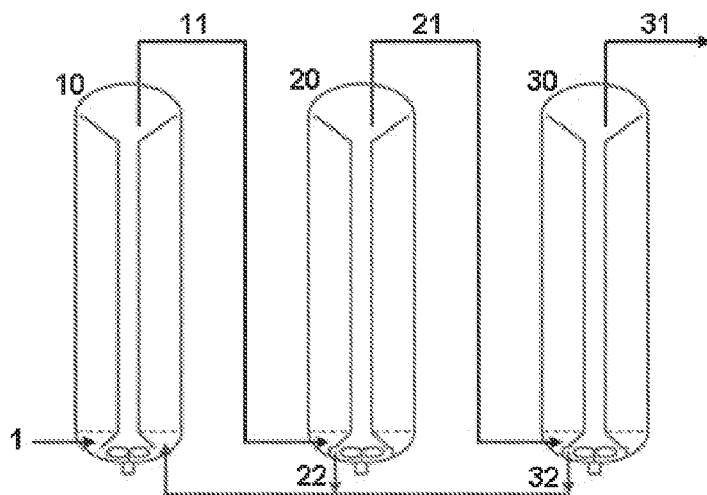


FIG. 1

(57) Abstract: Methods for hydroprocessing heavy oil feedstocks are disclosed. A heavy oil feedstock, a hydrogen-containing gas, and a slurry catalyst are passed through a plurality of upflow reactors operating under hydrocracking conditions to convert at least a portion of the heavy oil feedstock to lower boiling hydrocarbons, forming upgraded products. At least a portion of the mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst from an upflow reactor other than the first upflow reactor is sent back to at least one upstream upflow reactor as a recycled stream.

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

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

RECONFIGURATION OF RECIRCULATION STREAM IN UPGRADING HEAVY OIL

TECHNICAL FIELD

[001] This disclosure relates to methods for upgrading heavy oil feeds with a slurry catalyst composition.

BACKGROUND

[002] The petroleum industry is increasingly turning to heavy oil feeds such as heavy crudes, resids, coals, tar sands, etc., as sources for refining feedstocks for the manufacture of useful fuels. These feedstocks are characterized by high concentrations of asphaltenes rich residues and low API gravities, with some being as low as less than 0° API.

[003] Heavy oil feedstock typically contains high concentrations of heavy metals. Some of the heavy metals, such as nickel and vanadium, tend to react quickly, leading to deposition or trapping of vanadium-rich solids in processing equipment such as reactors. The solid deposition reduces available volume for reaction, which can significantly reduce the availability of a heavy oil feedstock processing system for the manufacture of commercial products.

[004] High shear rate and high catalyst content in a liquid recirculation reactor, e.g., an upflow reactor such as ebullating bed or slurry reactor, can reduce vanadium trapping during heavy oil upgrading. Unfortunately, control over these variables has been very limited to date. In ebullating bed reactors, which are typically equipped with either one internal or one external recirculation pump, liquid recirculation from the pump can provide the required shear and upflow. However, the shear rate must be high enough to fluidize or expand the catalyst bed, but not too high to carry over the catalyst into downstream reactor(s) and/or separator(s). In heavy oil feedstock upgrading processes that utilize slurry reactors, such an upper limit in recirculation rate is eliminated since the slurry catalyst flows with the liquid phase. However, the maximum recirculation rate in conventional slurry reactors is still determined by the capacity of the recirculation pump, since there is only a single pump used to provide recirculation in each reactor.

[005] In slurry reactors, the catalyst content in the front reactor can be increased by catalyst recycle. Conventionally, catalyst is directly recycled from the hot separator, but the amount of recycle catalyst is limited by the catalyst concentration in the hot separator, the slurry recycle rate and the overall heat balance. Other recycle modes can be used, such as

recycle after stripper bottoms product concentration, vacuum distillation or catalyst de-oiling, but these modes require larger downstream process units to prepare such recycle streams.

[006] There is still a need for improved methods to upgrade/treat process heavy oil feeds, particularly improved methods for better raw material utilization with less solid deposition.

SUMMARY

[007] In one aspect of the invention, there is provided a process for upgrading a heavy oil feedstock, the process employing a plurality of upflow reactors configured in series comprising a first upflow reactor and a last upflow reactor, the process comprising:

[008] combining a heavy oil feedstock, a hydrogen-containing gas, and a slurry catalyst in the first upflow reactor under hydrocracking conditions to convert at least a portion of the heavy oil feedstock to lower boiling hydrocarbons, forming upgraded products;

[009] passing a mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst sequentially through each subsequent upflow reactor, wherein each subsequent upflow reactor is maintained under hydrocracking conditions with additional hydrogen-containing gas to convert at least a portion of the heavy oil feedstock to lower boiling hydrocarbons, forming additional upgraded products;

[010] recycling at least a portion of the mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst from at least one upflow reactor other than the first upflow reactor mixture back to at least one upstream upflow reactor as a recycled stream; and

[011] passing a mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst from the last upflow reactor to a separator, whereby the upgraded products are removed with the hydrogen-containing gas as an overhead stream, and the slurry catalyst and the unconverted heavy oil feedstock are removed as a non-volatile stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[012] FIG. 1 is a flow diagram that schematically illustrates an embodiment of a heavy oil upgrade process with three upflow reactors configured in series.

DETAILED DESCRIPTION

[013] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[014] “Heavy oil” feed or feedstock refers to heavy and ultra-heavy crudes, including but not limited to resids, coals, bitumen, shale oils, tar sands, etc. Heavy oil feedstock can be liquid, semi-solid, and/or solid. Examples of heavy oil feedstock that can be upgraded as described herein include, but are not limited to, Canada tar sands, vacuum resid from Brazilian Santos and Campos basins, Egyptian Gulf of Suez, Chad, Venezuelan Zulua, Malaysia, and Indonesia Sumatra. Other examples of heavy oil feedstock include bottom of the barrel and residuum left over from refinery processes, including “bottom of the barrel” and “residuum” (or “resid”)—atmospheric tower bottoms, which have a boiling point of at least 343°C (650°F), or vacuum tower bottoms, which have a boiling point of at least 524°C (975°F), or “resid pitch” and “vacuum residue”—which have a boiling point of 524°C (975°F) or greater.

[015] Properties of heavy oil feedstock can include, but are not limited to: a TAN of at least 0.1 (e.g., at least 0.3, or at least 1); a viscosity of at least 10 mm²/s; and an API gravity of at most 20 (e.g., at most 10, or less than 5). A gram of heavy oil feedstock typically contains at least 0.0001 g of Ni/V/Fe; at least 0.005 g of heteroatoms; at least 0.01 g of residue; at least 0.04 g of C₅ asphaltenes; at least 0.002 g of Micro Carbon Residue (MCR) per g of crude; at least 0.00001 g of alkali metal salts of one or more organic acids; and at least 0.005 g of sulfur. In one embodiment, the heavy oil feedstock has a sulfur content of at least 5 wt. % and an API gravity of from −5 to +5.

[016] In one embodiment, the heavy oil feedstock comprises Athabasca bitumen (Canada) having at least 50% by volume vacuum resid. In another embodiment, the heavy oil feedstock is a Boscan (Venezuela) feed with at least 64% by volume vacuum residue. In one embodiment, the heavy oil feedstock contains at least 100 ppm V (per gram of heavy oil feedstock). In another embodiment, the V level ranges between 500 and 1000 ppm. In a third embodiment, the heavy oil feedstock contains at least 2000 ppm V.

[017] The terms “treatment,” “treated,” “upgrade,” “upgrading,” and “upgraded,” when used in conjunction with a heavy oil feedstock, describes a heavy oil feedstock that is being or has been subjected to hydroprocessing, or a resulting material or crude product, having a reduction in the molecular weight of the heavy oil feedstock, a reduction in the boiling point range of the heavy oil feedstock, a reduction in the concentration of asphaltenes,

a reduction in the concentration of hydrocarbon free radicals, and/or a reduction in the quantity of impurities, such as sulfur, nitrogen, oxygen, halides, and metals.

[018] The upgrade or treatment of heavy oil feeds can generally be referred herein as “hydroprocessing.” Hydroprocessing is meant as any process that is carried out in the presence of hydrogen, including, but not limited to, hydroconversion, hydrocracking, hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, hydrodearomatization, hydroisomerization, hydrodewaxing and hydrocracking including selective hydrocracking. The products of hydroprocessing can show improved viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization, etc.

[019] Heavy oil upgrading is utilized to convert heavy oil or bitumens into commercially valuable lighter products, e.g., lower boiling hydrocarbons including liquefied petroleum gas (LPG), gasoline, jet, diesel, vacuum gas oil (VGO), and fuel oils.

[020] “Hydrogen” refers to hydrogen, and/or a compound or compounds that when in the presence of a heavy oil feed and a catalyst react to provide hydrogen.

[021] “Slurry catalyst” (or sometimes referred to as “slurry” or “dispersed catalyst”) refers to a liquid medium, e.g., oil, water, or mixtures thereof, in which catalyst and/or catalyst precursor particles (aggregates, particulates or crystallites) are dispersed within. The term slurry catalyst refers to a fresh catalyst, or a catalyst that has been used in heavy oil upgrading and with diminished activity (not a fresh catalyst). A slurry catalyst can be a supported or an unsupported catalyst.

[022] “Fresh catalyst” refers to a catalyst or a catalyst precursor that has not been used in a reactor in a hydroprocessing operation. The term fresh catalyst herein also includes “re-generated,” “rehabilitated” or “recovered” catalysts, e.g., catalyst that has been used in at least a reactor in a hydroprocessing operation (“used catalyst”) but its catalytic activity has been restored or at least increased to a level well above the used catalytic activity level. The term “fresh catalyst” can be used interchangeably with “fresh slurry catalyst.”

[023] “Catalyst precursor” refers to a compound containing one or more catalytically active metals, from which compound a catalyst is eventually formed. It should be noted that a catalyst precursor can be catalytically active as a hydroprocessing catalyst. “Catalyst precursor” can be referred to herein as “catalyst” when used in the context of a catalyst feed.

[024] In one embodiment, the slurry catalyst feed stream contains a fresh catalyst in a medium (diluent). In another embodiment, the slurry catalyst feed contains a well-dispersed catalyst precursor composition capable of forming an active catalyst in situ within the feed

heaters and/or the contacting zone. The catalyst particles can be introduced into the medium (diluent) as powder in one embodiment, a precursor in another embodiment, or after a pre-treatment step in a third embodiment. In one embodiment, the medium (or diluent) is a hydrocarbon oil diluent. In another embodiment, the liquid medium is the heavy oil feedstock itself. In yet another embodiment, the liquid medium is a hydrocarbon oil other than the heavy oil feedstock, e.g., a VGO medium or diluent.

Heavy Oil Feedstock

[025] In one embodiment, the heavy oil feedstock suitable for use in hydroconversion processes disclosed herein is selected from the group consisting of atmospheric residuum, vacuum residuum, tar from a solvent deasphalting unit, atmospheric gas oils, vacuum gas oils, deasphalted oils, olefins, oils derived from tar sands or bitumen, oils derived from coal, heavy crude oils, synthetic oils from Fischer-Tropsch processes, and oils derived from recycled wastes and polymers. In the reactor, at least a portion of the heavy oil feedstock (higher boiling point hydrocarbons) is converted to lower boiling hydrocarbons, forming an upgraded product.

Slurry Catalyst

[026] The slurry catalyst is useful for, but not limited to, upgrading processes such as thermal hydrocracking, hydrotreating, hydrodesulfurization, hydrodenitrification, and hydrodemetallization. The catalyst can be used as the sole catalyst in the slurry hydroprocessing systems and in combination with other catalysts in other types of hydroprocessing systems such as processes employing fixed bed catalysts or ebullated bed catalysts. Some slurry catalysts suitable for use in the various embodiments of this invention are known in the art. See, e.g., U.S. Patent Nos. 7,396,799 and 7,410,928.

[027] In one embodiment, the slurry catalyst composition is prepared by a series of steps, involving mixing a Group VIB metal oxide, such as molybdenum, and aqueous ammonia to form an aqueous mixture, and sulfiding the mixture to form a slurry catalyst. The slurry catalyst is then promoted with a Group VIII metal. In one embodiment, the slurry catalyst is then mixed with a hydrocarbon oil and combined with hydrogen gas to produce an active slurry catalyst. In one embodiment, the slurry catalyst is kept mixed in storage until combined with feed in a hydroconversion process.

[028] In one embodiment, the slurry catalyst comprises catalyst particles (or particulates) having an average particle size of at least 1 micron in a hydrocarbon oil diluent. In another embodiment, the slurry catalyst comprises catalyst particles having an average particle size of from 1 to 20 microns (e.g., from 2 to 10 microns). In one embodiment, the

slurry catalyst comprises a catalyst having an average particle size ranging from colloidal (nanometer size) to 1 to 2 microns. In another embodiment, the slurry catalyst comprises a catalyst having extremely small particles that are molecular/colloidal in size (i.e., less than 100 nm, less than 10 nm, less than 5 nm, or less than 1 nm), which can aggregate into particles having an average size of from 1 to 10 microns in one embodiment, and from 1 to 20 microns in another embodiment, and less than 10 microns in yet a third embodiment.

[029] In one embodiment, a sufficient amount of slurry catalyst is fed to the reactor for each reactor to have a slurry (solid) catalyst concentration of at least 500 wppm to 3 wt. % (catalyst metal to heavy oil ratio). Catalyst metal refers to the active metal in the catalyst, e.g., for a NiMo sulfide slurry catalyst in which Ni is used as a promoter, the catalyst metal herein refers to the Mo concentration. In embodiments, the amount of catalyst feed in the reactor is from 500 to 7500 wppm of the catalyst metal in heavy oil feed (e.g., from 750 to 5000 wppm catalyst metal).

Heavy Oil Upgrade System

[030] In one embodiment for the upgrade of heavy oil feedstock, a plurality of upgrading reactors connected in series is employed, with the reactors being the same or different in configuration. Examples of reactors that can be used include stacked bed reactors, fixed bed reactors, ebullating bed reactors, continuously stirred tank reactors, fluidized bed reactors, spray reactors, liquid/liquid contactors, slurry reactors, liquid recirculation reactors, and combinations thereof. In one embodiment, the reactor is an upflow reactor.

[031] In embodiments, the process employs at least two upgrading reactors connected in series (e.g., at least three upgrading reactors connected in series, or at least four upgrading reactors connected in series).

[032] In the reactor, heavy hydrocarbon oil feedstock is admixed with a slurry feed comprising a catalyst and a hydrogen-containing gas at elevated pressure and temperature and hydroprocessed (preferably hydrocracked) for the removal of heteroatom contaminants, such as sulfur and nitrogen.

[033] In one embodiment, the upflow reactor includes a reactor outlet, a reactor inlet, a recirculation pump for generating a liquid recirculation flow rate, and at least one internal mixing device. The recirculation pump can be disposed within the upflow reactor itself or outside the upflow reactor.

[034] The hydroprocessing (or hydrocracking) can be practiced in either countercurrent flow mode, where the feedstream flows countercurrent to the flow of hydrogen-containing treat gas, or co-current flow mode.

[035] Process conditions in each upflow reactor include a temperature of from 392°F to 842°F (200°C to 450°C), a reactor pressure of from 1450 to 3626 psig (10 to 25 MPa), a liquid hourly space velocity of from 0.05 to 10 h⁻¹, and a hydrogen treat gas rate of from 300 to 10,000 SCF/bbl (53.4 to 1781 m³/m³).

[036] In the reactors under hydrocracking conditions, at least a portion of the heavy oil feedstock is converted to lower boiling hydrocarbons, forming upgraded products. The mixture of the upgraded products, the unconverted heavy oil feedstock, the slurry catalyst, the hydrogen-containing gas is sent to the next reactor in series, which is also maintained under hydrocracking conditions. In the next reactor with additional hydrogen-containing gas feed and optionally with additional heavy oil feedstock, at least a portion of the heavy oil feedstock is converted to lower boiling hydrocarbons, forming additional upgraded products.

[037] In the traditional configuration, the internal or external recirculation pump at each reactor delivers the slurry back to the same reactor. The slurry is only recirculated internally within the same reactor by the pump. In an embodiment of this invention, the recirculation pumps at downstream reactors (i.e., not the front-end or first reactor) send slurry to their upstream reactors. The slurry should have the same composition as the reactor that it originates from. The recirculation rate of the recycled stream from at least one downstream reactor is at least 3 times the rate of the incoming heavy oil feed stream (e.g., at least 5 times the rate of the incoming heavy oil feed stream). In embodiments, the recirculation rate of the recycled stream from at least one downstream reactor ranges from 3 to 15 times the rate of the incoming heavy oil feed stream (e.g., from 3 to 10 times the rate of the incoming heavy oil feed stream, from 3 to 8 times the rate of the incoming heavy oil feed stream, from 5 to 10 times the rate of the incoming heavy oil feed stream, or from 5 to 8 times the rate of the incoming heavy oil feed stream). In embodiments, it is believed that with higher recirculation rates provided by the recycle stream, heavy metals are passed through the system more quickly leading to less trapping or deposition on the processing equipment.

[038] In embodiments, the recycle stream is pumped to the first upflow reactor at a sufficient rate to provide a liquid superficial velocity in the first upflow reactor of greater than 6 cm/s (e.g., from 8 to 20 cm/s, from 10 to 20 cm/s, from 10 to 18 cm/s, from 12 to 20 cm/s, or from 12 to 18 cm/s).

[039] In embodiments, it is believed that with additional recycled catalyst provided by the recycled stream, more catalytic surface area (via the catalyst slurry in the recycled stream) is available to spread the heavy metal deposition, there is less trapping or deposition on the processing equipment. The additional catalyst surface area provided by the recycled

stream minimizes overloading the catalyst surface with heavy metal deposits, leading to reduced deposition on the processing equipment (walls, internal, etc.).

[040] In embodiments, the recycled stream contains from 0.3 to 30 wt. % of slurry catalyst (e.g., from 0.5 to 20 wt. % of slurry catalyst, or from 1 to 15 wt. % of slurry catalyst).

[041] In addition to the benefits of the higher recirculation rate (i.e., shear rate) and higher catalyst content which facilitate vanadium removal, the process disclosed herein has other positive operational benefits. Quench streams are typically added before reactors in conventional heavy oil upgrading processes to remove heat generated during hydrocracking. Since the inter-reactor flow is much higher in the process disclosed herein over conventional processes, the “hot” effluent from a reactor can be absorbed by the “cold” recycled feed thereby eliminating the need for conventional quench streams. Moreover, the less need for quench can also mean the less need for preheating a feed stream, since the large recycle stream provides the heat needed to reach a target temperature.

[042] In one embodiment, it is not necessary to recycle catalysts from the hot separator, vacuum distillation, or de-oiling unit, as in conventional heavy oil upgrading processes, eliminating the required high-temperature recycle pumps and other related equipment. In the process disclosed herein, catalyst recycling is realized by the existing recirculation pump for each reactor.

[043] In embodiments where the process disclosed herein employs at least two upgrading reactors connected in series, the last reactor is limited to recirculation from a single pump. Recirculation in any upstream reactor can come from two or more pumps. Therefore, loss of any single pump may not lead to a total loss of recirculation.

[044] In embodiments, a separation unit can be located between two upflow reactors, a prior upflow reactor and a subsequent upflow reactor. At least a portion of the mixture containing the upgraded products, unconverted heavy oil feedstock, slurry catalyst and hydrogen-containing gas is sent to the separator, e.g., an interstage flash separator (ISF), whereby upgraded products are removed with the hydrogen-containing gas as an overhead stream and the unconverted heavy oil feedstock and the slurry catalyst are removed as a non-volatile stream. In one embodiment, the process disclosed herein employs at least three upflow reactors and at least two separation units wherein at least one of the separation units zones is an ISF located in between two upflow reactors, a prior upflow reactor and a subsequent upflow reactor.

[045] Following the last reactor in any number of upflow reactors, a mixture containing the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing

gas, and the slurry catalyst is passed to a separator, whereby the upgraded products are removed with the hydrogen-containing stream as an overhead stream, and the slurry catalyst and the unconverted heavy oil feedstock are removed as a non-volatile stream.

[046] FIG. 1 is a schematic of an embodiment of a heavy oil upgrade process with three upflow reactors configured in series, e.g., reactors **10**, **20**, and **30**. Fresh feed **1** comprising a heavy oil feedstock, hydrogen-containing gas and slurry catalyst enters the bottom of reactor **10**. Effluent stream **11** comprising upgraded materials along with hydrogen-containing gas, slurry catalyst, and unconverted heavy oil exits the top of reactor **10** and is sent to the bottom of the next reactor **20** in series. A recycle stream **22** containing upgraded materials along with hydrogen-containing gas, slurry catalyst, unconverted heavy oil, is recycled back to the bottom of reactor **10**. Additional feedstream(s) containing hydrogen-containing gas, optional VGO feed, optional (additional) heavy oil feed, and optional catalyst feed can be combined with effluent stream **11** for further upgrade in reactor **20**.

[047] Effluent stream **21** comprising upgraded materials along with hydrogen-containing gas, slurry catalyst, and unconverted heavy oil exits the top of reactor **20** and is sent to the bottom of the next reactor **30** in series. A recycle stream **32** containing upgraded materials along with hydrogen-containing gas, slurry catalyst, unconverted heavy oil, is recycled back to the bottom of at least one of reactors **10** and **20**. Additional feedstream(s) containing hydrogen-containing gas, optional VGO feed, optional (additional) heavy oil feed, and optional catalyst feed can be combined with effluent stream **21** for further upgrade in reactor **30**.

[048] Effluent stream **31** comprising upgraded materials along with hydrogen-containing gas, slurry catalyst, and unconverted heavy oil exits the top of reactor **30** and is sent to a separator (not shown), e.g., a high pressure separator, wherein products and gases are separated from the non-volatile fraction, e.g., slurry catalyst and unconverted heavy oil.

EXAMPLES

[049] The following illustrative examples are intended to be non-limiting.

[050] A heavy oil upgrading process according to FIG. 1 (3 upflow reactors in series wherein both the second and the third reactor recirculation pumps discharge to the inlet of the first reactor and the third reactor recirculation pumps discharge to the inlet of the second reactor) was simulated and compared to a conventional heavy oil upgrading process as

described in U.S. Patent No. 7,390,398 (3 upflow reactors in series wherein only one pump is available for each reactor).

EXAMPLE 1

[051] The maximum liquid superficial velocity in each reactor of the process as described in U.S. Patent No. 7,390,398 was about 6 cm/s. In the process according to FIG. 1, the liquid superficial velocity can reach 18 cm/s in the first reactor and 12 cm/s in the second reactor, thus providing much higher shear rate to facilitate vanadium removal.

EXAMPLE 2

[052] With < 3000 ppm of Mo from fresh catalyst and once-through operation, the first reactor of the process as described in U.S. Patent No. 7,390,398 contains < 4000 ppm Mo or < 2 wt. % solids. In the process according to FIG. 1, all three reactors have essentially the same catalyst contents. At about 93% vacuum resid conversion, the first reactor can reach about 2.4 wt. % Mo or 12 wt. % solids, which is about six times that of the conventional design, while the second reactor will see the same benefit wherein the catalyst content is boosted about 3 to 4 times that of the conventional design.

EXAMPLE 3

[053] In the conventional process, the inter-reactor stream is cooled down by about 150°F to compensate for the highly exothermic consumption of about 700 SCF/bbl hydrogen. Assuming 8 times recirculation rate per fresh feed at each pump, there is only 9°F temperature increase between the first and second reactor in the configuration according to FIG. 1. The temperature rise from the second and third reactors will be about 17°F. Such a temperature profile is well within the current operating envelope and no quench is needed unless the reactors need to be operated more isothermally.

EXAMPLE 4

[054] In the conventional process such as described in U.S. Patent No. 7,390,398, fresh feed needs to be heated to about 700°F. In the process disclosed herein, the feed needs to be heated at 500°F to 600°F. Moreover, much less temperature increase along reactor height is observed. With recirculation pump within the same reactor, a large temperature increase is observed along reactor height. In the process according to FIG. 1, the temperature increase was reduced by $\frac{2}{3}$ and $\frac{1}{2}$ in the first and second reactors, respectively.

EXAMPLE 5

[055] In the conventional process, there can be up to a 20°F to 30°F temperature increase in the reactor when recirculation is provided by a single pump. In the process

according to FIG. 1, it is expected to that only about a 7°F to 10°F temperature increase and only about a 10°F to 15°F will be observed in the first and second reactors, respectively.

[056] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained. It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural references unless expressly and unequivocally limited to one referent. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items. As used herein, the term “comprising” means including elements or steps that are identified following that term, but any such elements or steps are not exhaustive, and an embodiment can include other elements or steps.

[057] Unless otherwise specified, the recitation of a genus of elements, materials or other components, from which an individual component or mixture of components can be selected, is intended to include all possible sub-generic combinations of the listed components and mixtures thereof.

[058] The patentable scope is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims. To an extent not inconsistent herewith, all citations referred to herein are hereby incorporated by reference.

CLAIMS

1. A process for upgrading a heavy oil feedstock, the process employing a plurality of upflow reactors configured in series comprising a first upflow reactor and a last upflow reactor, the process comprising:

combining a heavy oil feedstock, a hydrogen-containing gas, and a slurry catalyst in the first upflow reactor under hydrocracking conditions to convert at least a portion of the heavy oil feedstock to lower boiling hydrocarbons, forming upgraded products;

passing a mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst sequentially through each subsequent upflow reactor, wherein each subsequent upflow reactor is maintained under hydrocracking conditions with additional hydrogen-containing gas to convert at least a portion of the heavy oil feedstock to lower boiling hydrocarbons, forming additional upgraded products;

recycling at least a portion of the mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst from at least one upflow reactor other than the first upflow reactor mixture back to at least one upstream upflow reactor forming a recycled stream; and

passing a mixture comprising the upgraded products, unconverted heavy oil feedstock, the hydrogen-containing gas, and the slurry catalyst from the last upflow reactor to a separator, whereby the upgraded products are removed with the hydrogen-containing gas as an overhead stream, and the slurry catalyst and the unconverted heavy oil feedstock are removed as a non-volatile stream.

2. The process of claim 1, wherein the process employs at least two upflow reactors configured in series.

3. The process of claim 1, wherein liquid in the first upflow reactor is recirculated at a rate of from 3 to 15 times the rate of the heavy oil feedstock.

4. The process of claim 1, wherein liquid in the first upflow reactor is recirculated at a rate of from 3 to 10 times the rate of the heavy oil feedstock.

5. The process of claim 1, wherein the recycled stream from an upflow reactor other than the first upflow reactor is recirculated at a rate of from 3 to 15 the rate of the heavy oil feedstock.
6. The process of claim 1, wherein the recycled stream from an upflow reactor other than the first upflow reactor is recirculated at a rate of from 3 to 10 the rate of the heavy oil feedstock.
7. The process of claim 1, wherein the recycled stream comprises from 0.3 to 30 wt. % of slurry catalyst.
8. The process of claim 1, wherein the heavy oil feedstock is selected from the group consisting of atmospheric residuum, vacuum residuum, tar from a solvent deasphalting unit, atmospheric gas oils, vacuum gas oils, deasphalted oils, olefins, oils derived from tar sands or bitumen, oils derived from coal, heavy crude oils, synthetic oils from Fischer-Tropsch processes, and oils derived from recycled wastes and polymers.
9. The process of claim 1, wherein the slurry catalyst comprises catalyst particles having an average particle of from 1 to 20 microns.
10. The process of claim 1, wherein the hydrocracking conditions include a temperature of from 392°F to 842°F (200°C to 450°C), a reactor pressure of from 1450 to 3626 psig (10 to 25 MPa), a liquid hourly space velocity of from 0.05 to 10 h⁻¹, and a hydrogen treat gas rate of from 300 to 10,000 SCF/bbl (53.4 to 1781 m³/m³).

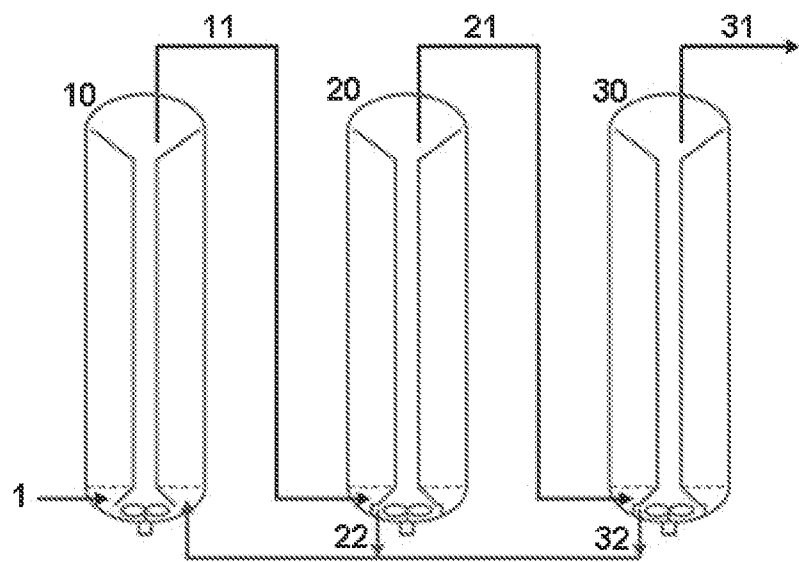


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/070711

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G65/10 C10G47/26
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G

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

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

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 7 390 398 B2 (FARSHID DARUSH [US] ET AL) 24 June 2008 (2008-06-24) cited in the application column 2, lines 6-36 column 2, line 49 - column 3, line 24; figure 1 column 4, lines 32-57 -----	1-10
Y	US 2007/140927 A1 (REYNOLDS BRUCE [US]) 21 June 2007 (2007-06-21) paragraph [[0017]] -----	3-6
X	US 2009/057195 A1 (POWERS CHRISTOPHER ALAN [US] ET AL) 5 March 2009 (2009-03-05) the whole document ----- -/-	1-10



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

27 May 2014

Date of mailing of the international search report

05/06/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Cagnoli, Michele

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/070711

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/138056 A1 (FARSHID DARUSH [US] ET AL) 21 June 2007 (2007-06-21)	1,2,7-10
Y	the whole document	3-6

X	US 6 139 723 A (PELRINE BRUCE P [US] ET AL) 31 October 2000 (2000-10-31)	1,2,7-10
Y	the whole document	3-6

X	US 6 190 542 B1 (COMOLLI ALFRED G [US] ET AL) 20 February 2001 (2001-02-20)	1,2,7-10
Y	the whole document	3-6

X	US 2007/138057 A1 (FARSHID DARUSH [US] ET AL) 21 June 2007 (2007-06-21)	1-10
	the whole document	

X	WO 2007/078622 A2 (CHEVRON USA INC [US]; FARSHID DARUSH [US]; REYNOLDS BRUCE [US]) 12 July 2007 (2007-07-12)	1,2,7-10
Y	the whole document	3-6

X	US 2007/138058 A1 (FARSHID DARUSH [US] ET AL) 21 June 2007 (2007-06-21)	1,2,7-10
Y	the whole document	3-6

X	US 2012/118791 A1 (CASH DENNIS R [US] ET AL) 17 May 2012 (2012-05-17)	1,2,7-10
Y	the whole document	3-6

X	US 5 871 638 A (PRADHAN VIVEK R [US] ET AL) 16 February 1999 (1999-02-16)	1,2,7-10
Y	the whole document	3-6

X	US 4 457 831 A (GENDLER JEFFREY L [US]) 3 July 1984 (1984-07-03)	1,2,7-10
Y	the whole document	3-6

X	US 3 215 617 A (BURCH WARREN E ET AL) 2 November 1965 (1965-11-02)	1,2,7-10
Y	the whole document	3-6

X	US 2007/138059 A1 (FARSHID DARUSH [US] ET AL) 21 June 2007 (2007-06-21)	1,2,7-10
Y	the whole document	3-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/070711

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7390398	B2	24-06-2008	BR PI0619921 A2 25-10-2011
		CA 2632823 A1 12-07-2007	
		CN 101360808 A 04-02-2009	
		EA 200870066 A1 27-02-2009	
		EP 1973995 A2 01-10-2008	
		JP 2009520061 A 21-05-2009	
		KR 20080077406 A 22-08-2008	
		US 2007138055 A1 21-06-2007	
		WO 2007078620 A2 12-07-2007	
US 2007140927	A1	21-06-2007	BR PI0619922 A2 25-10-2011
		CA 2632818 A1 12-07-2007	
		CN 101356001 A 28-01-2009	
		EA 200870065 A1 27-02-2009	
		EP 1960096 A2 27-08-2008	
		JP 5341520 B2 13-11-2013	
		JP 2009520060 A 21-05-2009	
		KR 20080077666 A 25-08-2008	
		US 2007140927 A1 21-06-2007	
		WO 2007078619 A2 12-07-2007	
US 2009057195	A1	05-03-2009	NONE
US 2007138056	A1	21-06-2007	BR PI0619988 A2 25-10-2011
		CA 2633902 A1 12-07-2007	
		CN 101336282 A 31-12-2008	
		EA 200870067 A1 30-12-2008	
		EP 1960498 A2 27-08-2008	
		JP 2009520062 A 21-05-2009	
		KR 20080077395 A 22-08-2008	
		US 2007138056 A1 21-06-2007	
		US 2009057194 A1 05-03-2009	
		WO 2007078621 A2 12-07-2007	
US 6139723	A	31-10-2000	NONE
US 6190542	B1	20-02-2001	NONE
US 2007138057	A1	21-06-2007	US 2007138057 A1 21-06-2007
			US 2009057193 A1 05-03-2009
WO 2007078622	A2	12-07-2007	NONE
US 2007138058	A1	21-06-2007	CN 101356252 A 28-01-2009
			US 2007138058 A1 21-06-2007
US 2012118791	A1	17-05-2012	NONE
US 5871638	A	16-02-1999	NONE
US 4457831	A	03-07-1984	CA 1229570 A1 24-11-1987
		DE 3327842 A1 12-07-1984	
		JP H0765056 B2 12-07-1995	
		JP S5945390 A 14-03-1984	
		US 4457831 A 03-07-1984	
US 3215617	A	02-11-1965	NONE

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/070711

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007138059 A1	21-06-2007	BR PI0619931 A2	25-10-2011
		CA 2631855 A1	12-07-2007
		EA 200870068 A1	30-12-2009
		EP 1960499 A2	27-08-2008
		JP 5081160 B2	21-11-2012
		JP 2009520063 A	21-05-2009
		JP 2012255158 A	27-12-2012
		KR 20080080618 A	04-09-2008
		US 2007138059 A1	21-06-2007
