



- (51) **International Patent Classification:**
C10G 47/00 (2006.01) *C10G 55/04* (2006.01)
- (21) **International Application Number:**
PCT/US2012/041643
- (22) **International Filing Date:**
8 June 2012 (08.06.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
13/156,487 9 June 2011 (09.06.2011) US
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(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, 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, IS, JP, KE, KG, KM, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— 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))

(54) **Title:** PROCESS COMPRISING HYDROCRACKING AND HYDRODESULFURISATION STEP OF A HYDROCARBON FEEDSTOCK FOLLOWED BY FLASH DISTILLATION

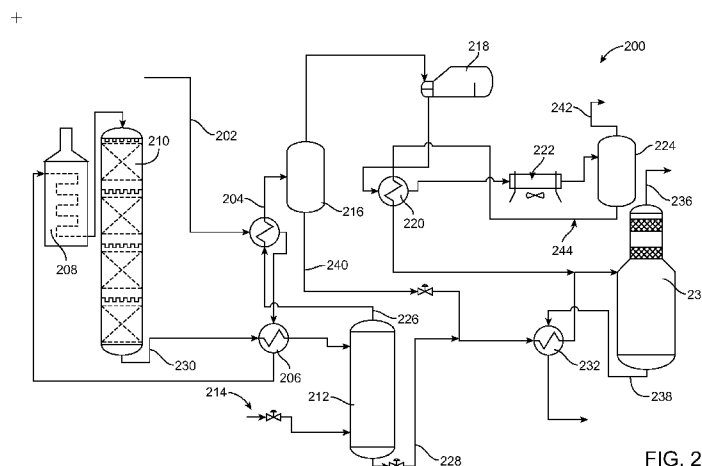


FIG. 2

(57) **Abstract:** According to one embodiment, a method includes desulfurizing a hydrocarbon feedstock in the presence of a desulfurization catalyst. A hydrocarbon product is recovered. The color of the hydrocarbon product is improved and the sulfur content of the hydrocarbon product is reduced by flash distilling the product.

PROCESS COMPRISING HYDROCRACKING AND HYDRODESULFURISATION STEP OF A HYDROCARBON FEEDSTOCK FOLLOWED BY FLASH DISTILLATION

FIELD OF TECHNOLOGY

5 [0001] The present application is directed to systems and methods for processing hydrocarbons.

BACKGROUND

10 [0002] The petroleum refining industry encounters many stringent environmental and market demands for cleaner and more purified fractions of fuels. Hydrotreating and hydrocracking can be used to remove sulfur and convert heavy hydrocarbons into a broad range of lighter hydrocarbon fractions.

15 [0003] Hydrocracking is typically a two-stage process combining sulfur removal, catalytic cracking and hydrogenation. In a hydrotreating stage, sulfur is removed from feedstock. In a cracking stage, heavier components of feedstock are cracked in the presence of hydrogen to produce more desirable products. The process employs high pressure, high temperature, a catalyst and hydrogen.

[0004] A wide variety of process flow schemes, operating conditions and catalysts have been used in commercial hydrocracking processes. However, systems and methods which provide improved product yield and improved catalyst characteristics are needed in the field of art.

SUMMARY

20 [0005] Systems and methods for processing hydrocarbons are herein disclosed. According to one embodiment, a method includes desulfurizing a hydrocarbon feedstock in the presence of a desulfurization catalyst. A hydrocarbon product is recovered. The color of the hydrocarbon product is improved and the sulfur content of the hydrocarbon product is reduced by flash distilling the product.

25 [0006] The foregoing and other objects, features and advantages of the present disclosure will become more readily apparent from the following detailed description of exemplary embodiments as disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

30 [0007] Embodiments of the present application are described, by way of example only, with reference to the attached Figures, wherein:

[0008] FIG. 1 illustrates an exemplary system for hydrocracking hydrocarbons according to

one embodiment;

[0009] FIG. 2 illustrates an exemplary system for hydrotreating hydrocarbons according to one embodiment; and

[0010] FIG. 3 illustrates an exemplary system for processing ultra low sulfur diesel according to one embodiment.

DETAILED DESCRIPTION

[0011] It will be appreciated that for simplicity and clarity of illustration, where considered appropriate, reference numerals may be repeated among the figures to indicate corresponding or analogous elements. In addition, numerous specific details are set forth in order to provide a thorough understanding of the example embodiments described herein. However, it will be understood by those of ordinary skill in the art that the example embodiments described herein may be practiced without these specific details. In other instances, methods, procedures and components have not been described in detail so as not to obscure the embodiments described herein.

[0012] The feedstock for the systems and methods disclosed herein can include, but are not limited to hydrocarbons, organic materials, mineral oils, synthetic oils, shale oils, tar sands, atmospheric gas oils, vacuum gas oils, deasphalted residua, vacuum residue, atmospheric residua, hydrotreated residual oils, coker distillates, straight run distillates, pyrolysis-derived oils, high boiling synthetic oils, cycle oils, cat cracker distillates, diesel, ultra low sulfur diesel and fractions and mixtures thereof.

[0013] FIG. 1 illustrates an exemplary system for hydrocracking hydrocarbons according to one embodiment. A feed stream can include, but is not limited to hydrocarbons, organic materials, mineral oils, synthetic oils, shale oils, tar sands, atmospheric gas oils, vacuum gas oils, deasphalted residua, vacuum residue, atmospheric residua, hydrotreated residual oils, coker distillates, straight run distillates, pyrolysis-derived oils, high boiling synthetic oils, cycle oils, cat cracker distillates or fractions and mixtures thereof.

[0014] The feed stream is provided via line 1 and is mixed with hydrogen gas provided via line 36. The resulting mixture is introduced into a hydrocracking zone 3 via line 2. The hydrocracking zone 3 can include one or more reactors containing one or more beds of the same or different hydrocracking catalysts used to hydrocrack the feed stream.

[0015] The hydrocracking catalyst can include, but is not limited to amorphous bases and low-level zeolite bases combined with one or more Group VIII or Group VIB metal hydrogenating components. The hydrocracking catalyst can also include, but is not limited to

any crystalline zeolite cracking base with a Group VIII metal hydrogenating component deposited within the zeolite. Additional hydrogenating components can be selected from Group VIB metal hydrogenating components for incorporation with the zeolite base.

5 **[0016]** Zeolite cracking bases can be referred to as molecular sieves and are usually composed of silica, alumina and one or more exchangeable cations such as sodium, magnesium, calcium or rare earth metals. Suitable zeolites found in nature include, for example, mordenite, stilbite, heulandite, ferrierite, dachiardite, chabazite, erionite and faujasite. Suitable synthetic zeolites include, for example, the B, X, Y and L crystal types, e.g., synthetic faujasite and mordenite.

10 **[0017]** The active metal hydrogenation components used in hydrocracking catalysts herein disclosed can include, but are not limited to Group VIII components including iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. In addition to these metals, other promoters can also be used in conjunction therewith, including Group VIB metals such as, molybdenum and tungsten.

15 **[0018]** The amount of hydrogenating metal in the catalyst can vary within wide ranges. In an exemplary embodiment, any amount between about 0.05 percent and 30 percent by weight can be used and in the case of noble metals an amount between about 0.05 to about 2 weight percent can be used. The hydrogenating metal can be incorporated into the hydrocracking catalyst by contacting a zeolite base material with an aqueous solution of desired metal in
20 cationic form. Following addition of the selected hydrogenating metal or metals, the resulting catalyst powder can be filtered, dried, pelleted and calcined in air at temperatures of, for example, 371 to 648°C in order to activate the catalyst and decompose ammonium ions.

25 **[0019]** The zeolite component can also first be pelleted, followed by the addition of the hydrogenating component and activation by calcining. The hydrocracking catalysts can be used in undiluted form or the powdered zeolite catalyst can be mixed and copelleted with other relatively less active catalysts, diluents or binders such as alumina, silica gel, silica-alumina cogels, activated clays and the like. These diluents can contain a minor proportion of an added hydrogenating metal such as a Group VIB and/or Group VIII metal.

30 **[0020]** The hydrocracking of the feed stream occurs by contacting the hydrocracking catalyst with the feed stream in the presence of hydrogen in the hydrocracking zone 3. The hydrocracking of the feed stream breaks carbon-carbon bonds within the feed stream.

[0021] In an exemplary embodiment, hydrocracking herein disclosed can occur at the following range of operating conditions:

Temperature:	250-460°C
Pressure:	8-200 bar
Liquid Hourly Space Velocity:	0.1-30 hr ⁻¹
H ₂ /Hydrocarbon Ratio:	3,000-10,000 SCFB
5 H ₂ Consumption:	1,200-3,500 SCFB

[0022] The hydrocracked feed stream can be introduced into a hot, high pressure stripper 5 via line 4. The stripper 5 can be maintained at essentially the same pressure as the hydrocracking zone 3 and a temperature from about 232-468°C. The feed stream is contacted with a counter-current flow of hydrogen gas or a hydrogen-rich gas stream to produce an overhead vapor hydrocarbon stream comprising diesel boiling range hydrocarbons and a bottom liquid hydrocarbon stream comprising hydrocarbons with a higher boiling point than the overhead vapor hydrocarbon stream.

[0023] The bottom liquid hydrocarbon stream is carried via line 6 and introduced into hot flash drum 7 to produce a vapor stream carried via line 8. The vapor stream carried via line 8 can be cooled in a heat exchanger (not shown) and the resulting cooled stream can be introduced into cold flash drum 11 via lines 8 and 10.

[0024] The overhead vapor hydrocarbon stream is carried via line 24 and can be mixed with a hydrocarbon stream carried via line 39. The resulting mixed vapor hydrocarbon stream is carried via line 25 and introduced into a desulfurization zone 26. The desulfurization zone 26 can include one or more reactors containing one or more beds of the same or different desulfurization catalysts used to remove sulfur from the mixed vapor hydrocarbon stream.

[0025] The desulfurization catalyst can include, but is not limited to hydrocracking catalysts herein disclosed including at least one Group VII metal component such as, iron, cobalt and/or nickel and at least one Group VI metal such as, molybdenum and/or tungsten, on a high surface area support material, such as alumina. Other suitable desulfurization catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from palladium and platinum. More than one type of desulfurization catalyst can be used in the same reaction vessel or zone.

[0026] In an exemplary embodiment, the Group VIII metal is typically present in an amount ranging from about 2 to about 20 weight percent. The Group VI metal is typically present in an amount ranging from about 1 to about 25 weight percent.

[0027] The desulfurization of the mixed vapor hydrocarbon stream carried via line 25 occurs by contacting the desulfurization catalyst with the mixed vapor hydrocarbon stream in

the desulfurization zone 26. The desulfurization of the mixed vapor hydrocarbon stream removes sulfur from the mixed vapor hydrocarbon stream. The desulfurization catalyst can also be contacted with the mixed vapor hydrocarbon stream to remove nitrogen, saturate aromatics and improve cetane.

5 **[0028]** In an exemplary embodiment, desulfurization can occur at the following range of operating conditions:

Temperature: 200-485°C

Pressure: 8-200 bar

Liquid Hourly Space Velocity: $0.1-10 \text{ hr}^{-1}$

10 **[0029]** The resulting desulfurization effluent is carried via line 27 and is introduced into a high pressure separator 28. A hydrogen-rich vapor is removed from the high pressure separator via line 29 and introduced into acid recovery zone 30. A lean solvent can be introduced via line 31 into acid gas recovery zone 30 to contact the hydrogen-rich vapor stream and dissolve acid gas therein. A rich solvent containing acid gas can be removed from the acid gas recovery zone
15 via line 32 for recovery. A hydrogen-rich vapor stream containing a reduced concentration of acid gas is removed from the acid gas recovery zone 30 via line 33. The hydrogen-rich vapor stream can be mixed with a hydrogen make-up stream via line 34 and the resulting mixture can be carried via line 35. The hydrogen-rich vapor stream carried via line 35 can be bifurcated. A first stream can be carried via line 36 and introduced into the hydrocracking zone 3 via line 2
20 and a second stream can be carried via line 37 and introduced as stripping gas into the hot, high pressure stripper 5.

[0030] As previously described, the bottom liquid hydrocarbon stream is carried via line 6 from the hot, high pressure stripper 5 and introduced into hot flash drum 7 to produce a vapor stream carried via line 8. The vapor stream carried via line 8 can be cooled in a heat exchanger (not shown) and the resulting cooled stream can be introduced into cold flash drum 11 via lines 8 and 10.

[0031] A liquid hydrocarbon stream is removed from high pressure separator 28 and transported via lines 9 and 10 and introduced into cold flash drum 11. A vapor hydrocarbon stream is removed from cold flash drum 11 via line 12 and recovered. A liquid stream is removed from cold flash drum 11 via line 13 and introduced into stripper 14. A vapor stream is removed from stripper 14 via line 15 and recovered.

[0032] A liquid hydrocarbon stream is removed from stripper 14 via line 16 and introduced into a first section of a distillation column 17. Naphtha hydrocarbon streams can be removed from the distillation column 17 via line 18 and recovered. Kerosene boiling range hydrocarbon

streams can be removed from the distillation column 17 via line 19 and recovered. Low sulfur diesel boiling range hydrocarbon vapor streams can be removed from the distillation column 17 via line 20 and recovered.

5 [0033] A liquid hydrocarbon stream can be removed from hot flash drum 7 via line 21 and introduced into a second section of the distillation column 17 to produce a liquid hydrocarbon stream containing diesel boiling range hydrocarbons, which is removed from the distillation column 17 via line 22. The hydrocarbon stream carried via line 22 can be mixed with a second feed stream which is introduced via line 38 and the resulting mixture can be carried via lines 39 and 25 and introduced into desulfurization zone 26. A liquid stream containing ultra low sulfur 10 diesel boiling range product can be removed from the bottoms of the distillation column 17 via line 23 and recovered for further processing as disclosed with respect to FIG. 3 below.

[0034] It will be understood by those of ordinary skill in the art that the hydrocracking and desulfurization processes herein disclosed can include modifications, additional features and additional components. For example, in other commercial hydrocracking processes 15 desulfurization of the hydrocarbon feedstock can occur prior to, after or concurrently with hydrocracking of the feedstock.

[0035] In an exemplary embodiment, the hydrocracking of a hydrocarbon feedstock is a two stage process wherein desulfurization occurs prior to hydrocracking. Preheated feedstock is mixed with recycled hydrogen and sent to a first-stage reactor, where catalysts convert sulfur and nitrogen compounds to hydrogen sulfide and ammonia. In the first stage, limited to no 20 hydrocracking occurs. After the hydrocarbon mixture leaves the first stage, it is cooled and liquefied and run through a hydrocarbon separator. Hydrogen gas is recycled for mixing with additional feedstock and a liquid hydrocarbon stream is charged to a fractionator. Depending on the desired products and product specification, the fractionator is run to eliminate particular components from the first stage reactor out-turn. Kerosene-range material can be taken as a 25 separate side-draw product or included in the fractionator bottoms. The fractionator bottoms can be mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking, and reforming in the first stage, the operations of the second stage are more severe (higher temperatures and pressures). Like the 30 outturn of the first stage, the second stage product is separated from the hydrogen and charged to the fractionator. A diesel range hydrocarbon product can be recovered from this two-stage process for further processing as disclosed with respect to FIG. 3 below.

[0036] FIG. 2 illustrates an exemplary system 200 for hydrotreating hydrocarbons according to one embodiment. A feed stream 202 can include, but is not limited to hydrocarbons, organic

materials, mineral oils, synthetic oils, shale oils, tar sands, atmospheric gas oils, vacuum gas oils, deasphalted residua, vacuum residue, atmospheric residua, hydrotreated residual oils, coker distillates, straight run distillates, pyrolysis-derived oils, high boiling synthetic oils, cycle oils, cat cracker distillates or fractions and mixtures thereof.

5 **[0037]** The feed stream 202 can be heated in a series of heat exchangers 204, 206 and a furnace 208 before it is introduced into a hydrotreating desulfurization zone 210. The desulfurization zone 210 can include one or more reactors containing one or more beds of the same or different desulfurization catalysts.

[0038] The desulfurization catalyst can include, but is not limited to hydrocracking catalysts herein disclosed including at least one Group VII metal component such as, iron, cobalt and/or nickel and at least one Group VI metal such as, molybdenum and/or tungsten, on a high surface area support material, such as alumina. Other suitable desulfurization catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from palladium and platinum. More than one type of desulfurization catalyst can be used in the same reaction vessel or zone to remove sulfur from the feed stream 202. In an exemplary embodiment, the desulfurization catalyst is a nickel molybdenum catalyst.

[0039] The desulfurization of the feed stream 202 occurs by contacting the desulfurization catalyst with the feed stream 202 in the desulfurization zone 210. The desulfurization of the feed stream 202 reduces the sulfur content of the feed. The desulfurization catalyst can also be contacted with the feed stream 202 to remove nitrogen, saturate aromatics and improve cetane. Typically, limited to no cracking occurs in the desulfurization zone 210 in the system 200. However, it is contemplated that substantial cracking of the feed stream 202 could also occur in the desulfurization zone 210 depending on the desulfurization catalyst, operating temperature and pressure used within the desulfurization zone 210.

25 **[0040]** In an exemplary embodiment, desulfurization can occur at the following range of operating conditions:

Temperature: 200-485°C

Pressure: 8-200 bar

Liquid Hourly Space Velocity: 0.1-10 hr⁻¹

30 **[0041]** A desulfurized feed stream 230 can be introduced into a stripper 212. Hydrogen gas or a hydrogen-rich gas stream can also be introduced into the stripper 212 from a hydrogen gas source 214. The desulfurized feed stream 230 is contacted with a counter-current flow of hydrogen gas or a hydrogen-rich gas to produce an overhead stream 226 and a bottoms stream 228.

[0042] The overhead stream is a sour gas stream 226 that can contain sulfur, hydrogen, methane, ethane, hydrogen sulfide, NH_3 , propane, butane, heavier components and/or other impurities. The overhead sour gas stream 226 can be cooled by exchanging heat with the feed stream 202 in a heat exchanger 204, thereby cooling and/or condensing the overhead sour gas stream 226 and heating the feed stream 202. The cooled, condensed or partially condensed overhead sour gas stream can be flashed in a hot flash drum 216, further cooled in a heat exchanger 220 and one or more hot flash vapor coolers 218, 222 and flashed in a cold flash drum 224.

[0043] A bottoms stream 240 containing hydrocarbons can be taken from the hot flash drum 216, cooled in a heat exchanger 232 and fed to a product fractionator 234 or distillation column 234 for separation into component parts. An overhead stream 242 of sour hydrogen gas can be taken from the cold flash drum 224. A bottoms stream 244 containing hydrocarbons can be taken from the cold flash drum 224, heated in a heat exchanger 220 and fed to a product fractionator 234 or distillation column 234 for separation into component parts.

[0044] The bottoms stream 228 from the stripper 212 is a hydrocarbon product stream 228. The hydrocarbon product stream can be cooled in a heat exchanger 232 and separated into various hydrocarbon fractions in a product fractionator 234 or distillation column 234 to produce an overhead stream 236 within the naphtha boiling point range and a bottoms stream product 238 within the diesel boiling point range, such as an ultra low sulfur diesel (ULSD) recovered for further processing as disclosed with respect to FIG. 3 below.

[0045] The hydrocracking and hydrotreating processes herein disclosed (e.g., as shown in FIGS. 1-2) can produce ULSD products. However, the hydrocracking and desulfurization catalysts must be changed frequently when the color of ULSD exceeds the specification target. Although the catalyst may still be active in removing sulfur, the color ULSD can be off-specification.

[0046] In an exemplary embodiment, the color of the ULSD cannot exceed 2.5 ASTM and when exceeded the hydrocracking catalyst and/or the desulfurization catalyst will have more than or equal to 5 months until deactivation. The exemplary systems herein disclosed for processing ULSD can improve the color of a hydrocarbon product comprising diesel within a required specification as determined by ASTM standards.

[0047] FIG. 3 illustrates an exemplary system for processing ULSD according to one embodiment. ULSD produced from a hydrocracking or hydrotreating process is provided as feedstock for the system. In an exemplary embodiment, the ULSD feed contains less than or equal to 20 ppm sulfur and more preferably less than or equal to 10 ppm sulfur.

[0048] ULSD is provided from a fractionator or distillation column of a hydrocracking or hydrotreating process described herein and introduced into a heat exchanger 102 via line 100 for heating. In an exemplary embodiment, ULSD enters the heat exchanger 102 at an inlet temperature of 238°C and is heated to an outlet temperature of 324°C.

5 [0049] ULSD exits the heat exchanger 102 and is introduced into a furnace 108 via lines 104 and 106 for further heating. In an exemplary embodiment, ULSD enters the furnace 108 at an inlet temperature of 324°C and is heated to an outlet temperature of 366°C.

[0050] Heated ULSD is introduced into a flash distillation tank 110 and the ULSD is distilled or flash vaporized to separate impurities and colorants from the ULSD. The bottoms stream
10 from the flash distillation tank 110 can comprise heavy diesel, colorants, sulfur and /or other impurities. In an exemplary embodiment, the bottoms stream of the flash distillation tank 110 contains 1% or less by weight heavy diesel with the remainder of the composition comprising colorants and sulfur.

[0051] The bottoms stream from the flash distillation tank 110 can be carried via line 112 for
15 additional processing. In additional processing steps, the bottoms stream from the flash distillation tank 110 can be recovered for further processing.

[0052] The overhead product of the flash distillation tank 110 comprises ULSD having improved color within specification as determined by ASTM standards. In an exemplary embodiment, the overhead product is 99 percent by weight pure diesel having a color of less
20 than or equal to 2.5 as determined by ASTM standards. In another exemplary embodiment, the overhead product is 99 percent by weight pure diesel having a color of less than or equal to 1.5 as determined by ASTM standards.

[0053] The overhead product of the flash distillation tank 110 can be carried via line 114 into the heat exchanger 102 and used as heating fluid for heating the ULSD feedstock. The
25 overhead product of the flash distillation tank 110 is cooled in the heat exchanger 102 as heat is exchanged between the ULSD feedstock and the overhead product of the flash distillation tank 110. The overhead product of the flash distillation tank 110 can be carried via line 116 and introduced into a secondary heat exchanger 118 for further cooling. The cooled product can be introduced into a surge tank 122 via line 120. Excess gas, such as hydrogen gas and nitrogen
30 gas can be removed from the product and vented in an overhead stream flowing from the surge tank 122. The bottoms product of the surge tank can be pumped via pump 124 and carried via line 126 for further cooling, processing and recovery.

[0054] The systems and methods herein disclosed for processing ULSD can be used to

improve the color quality of ULSD. In an exemplary embodiment, the color of an off-specification ULSD feedstock provided from a hydrocracking process can be improved from 5.6 to 1.5 as measure by ASTM standards by flash distilling the ULSD feedstock as disclosed herein.

- 5 **[0055]** The systems and methods herein disclosed for processing ULSD can also reduce the sulfur concentration of ULSD. In exemplary embodiments, flash distillation of a ULSD feedstock reduced the sulfur concentration of the ULSD feedstock between about 20 percent by weight to about 40 percent by weight reduction in sulfur. The hydrocracking or hydrotreating process from which the ULSD feedstock is produced can be conducted at lower temperatures and yield products with higher sulfur content due to the additional reduction in sulfur obtained from flash distilling the ULSD feedstock as disclosed herein. The life of the hydrocracking catalysts and the desulfurization catalysts is extended by conducting hydrocracking at lower temperatures. Additionally, deeper cuts or fractions of light cycle oil (LCO) can be produced in the hydrocracking or hydrotreating process from which the ULSD feedstock is produced.
- 10
- 15 **[0056]** The systems and methods herein disclosed for processing ULSD can also improve API Gravity. In an exemplary embodiment, the API Gravity of ULSD is increased by about 0.3 by flash distilling the ULSD feedstock as disclosed herein.

EXAMPLES

- 20 **[0057]** The following examples are provided for illustrative purposes. The examples are not intended to limit the scope of the present disclosure and they should not be so interpreted.

- 25 **[0058]** A ULSD feedstock from a hydrotreating process was used in the illustrative Examples herein disclosed. The feedstock was heated to a temperature of 366°C with the use of a heat exchanger and furnace as described with respect to FIG. 2. The feedstock was fed into a flash distillation tank and flashed distilled in order to remove impurities including colorants, sulfur and other impurities. The overhead ULSD product from the flash distillation tank was recovered and the bottoms stream impurities from the flash distillation tank were further processed as described with respect to FIG. 2. The product exhibited improved color and reduced sulfur content. The color and sulfur content for three exemplary ULSD feed compositions before and after flash distillation are provided in Tables 1 and 2.

Table 1: Color Improvement of ULSD

Feed	Feed Color (ASTM)	Product Color (ASTM)
Feedstock 1	5.2	1.1
Feedstock 2	3.7	0.6
Feedstock 3	3.3	0.4
Feedstock 4	3.5	0.5
Feedstock 5	2.7	0.5
Feedstock 6	5.1	0.4
Feedstock 7	3.9	0.3

Table 2: Sulfur Content Reduction of ULSD

Feed	Feed S Content (ppm)	Product S Content (ppm)	Sulfur Reduction (weight percent)
Feedstock 1	9.5	5.7	40%
Feedstock 7	25	13.1	48%
Feedstock 8	6.9	5.2	25%
Feedstock 9	6.9	2.8	59%
Feedstock 10	6.1	5.4	12%

- 5 **[0059]** As illustrated in Table 1, the color of Feedstock 1 was improved from 5.2 to 1.1; the color of Feedstock 2 was improved from 3.7 to 0.6; the color of Feedstock 3 was improved from 3.3 to 0.4; the color of Feedstock 4 was improved from 3.5 to 0.5; the color of Feedstock 5 was improved from 2.7 to 0.5; the color of Feedstock 6 was improved from 5.1 to 0.4; and the color of Feedstock 7 was improved from 3.9 to 0.3.
- 10 **[0060]** As illustrated in FIG. 2, the sulfur content of Feedstock 1 was reduced by 40 percent by weight; the sulfur content of Feedstock 7 was reduced by 48 percent by weight; the sulfur content of Feedstock 8 was reduced by 25 percent by weight, the sulfur content of Feedstock 9 was reduced by 59 percent by weight; and the sulfur content of Feedstock 10 was reduced by 12 percent by weight.
- 15 **[0061]** Example embodiments have been described hereinabove regarding improved systems and methods for processing hydrocarbons. Various modifications to and departures from the disclosed example embodiments will occur to those having ordinary skill in the art. The subject matter that is intended to be within the spirit of this disclosure is set forth in the following claims.

CLAIMS

What is claimed is:

1. A method for processing a hydrocarbon feedstock comprising:
desulfurizing a hydrocarbon feedstock in the presence of a desulfurization catalyst;
5 recovering a hydrocarbon product; and
improving the color of the hydrocarbon product and reducing the sulfur content of the
hydrocarbon product by flash distilling the hydrocarbon product.
2. The method as recited in claim 1, further comprising hydrocracking the hydrocarbon feedstock
10 in the presence of hydrogen and a hydrocracking catalyst.
3. The method as recited in claim 1, wherein the feedstock comprises hydrocarbons with a
boiling point above the diesel boiling range.
- 15 4. The method as recited in claim 1, wherein the hydrocarbon product comprises diesel.
5. The method as recited in claim 1, wherein the hydrocarbon product comprises greater than or
equal to 75 percent by weight diesel.
- 20 6. The method as recited in claim 1, wherein the color of the hydrocarbon product is improved to
a color of less than or equal to 2.5 as determined by ASTM standards.
7. The method as recited in claim 1, wherein the color of the hydrocarbon product is improved to
a color of less than or equal to 1.5 as determined by ASTM standards.
- 25 8. The method as recited in claim 1, wherein flash distilling the hydrocarbon product reduces the
sulfur content of the hydrocarbon product.
9. The method as recited in claim 8, wherein the sulfur content of the hydrocarbon product is
30 reduced by less than or equal to 40 percent by weight of the total hydrocarbon product.
10. The method as recited in claim 8, wherein the sulfur content of the hydrocarbon product is
reduced by greater than or equal to 40 percent by weight of the total hydrocarbon product

11. The method as recited in claim 1, wherein flash distilling the hydrocarbon product generates an overhead hydrocarbon stream comprising 99 percent by weight diesel.
12. The method as recited in claim 2, wherein hydrocracking the hydrocarbon feedstock occurs
5 prior to desulfurizing the hydrocarbon feedstock.
13. The method as recited in claim 2, wherein desulfurizing the hydrocarbon feedstock occurs prior to hydrocracking the hydrocarbon feedstock.
- 10 14. The method as recited in claim 2, wherein desulfurizing the hydrocarbon feedstock occurs concurrently to hydrocracking the hydrocarbon feedstock.
15. The method as recited in claim 2, wherein the hydrocracking catalyst and the desulfurization catalyst are the same.
15
16. The method as recited in claim 2, wherein the hydrocracking catalyst and the desulfurization catalyst are dissimilar.
17. The method as recited in claim 1, wherein the desulfurization catalyst is a nickel
20 molybdenum catalyst.

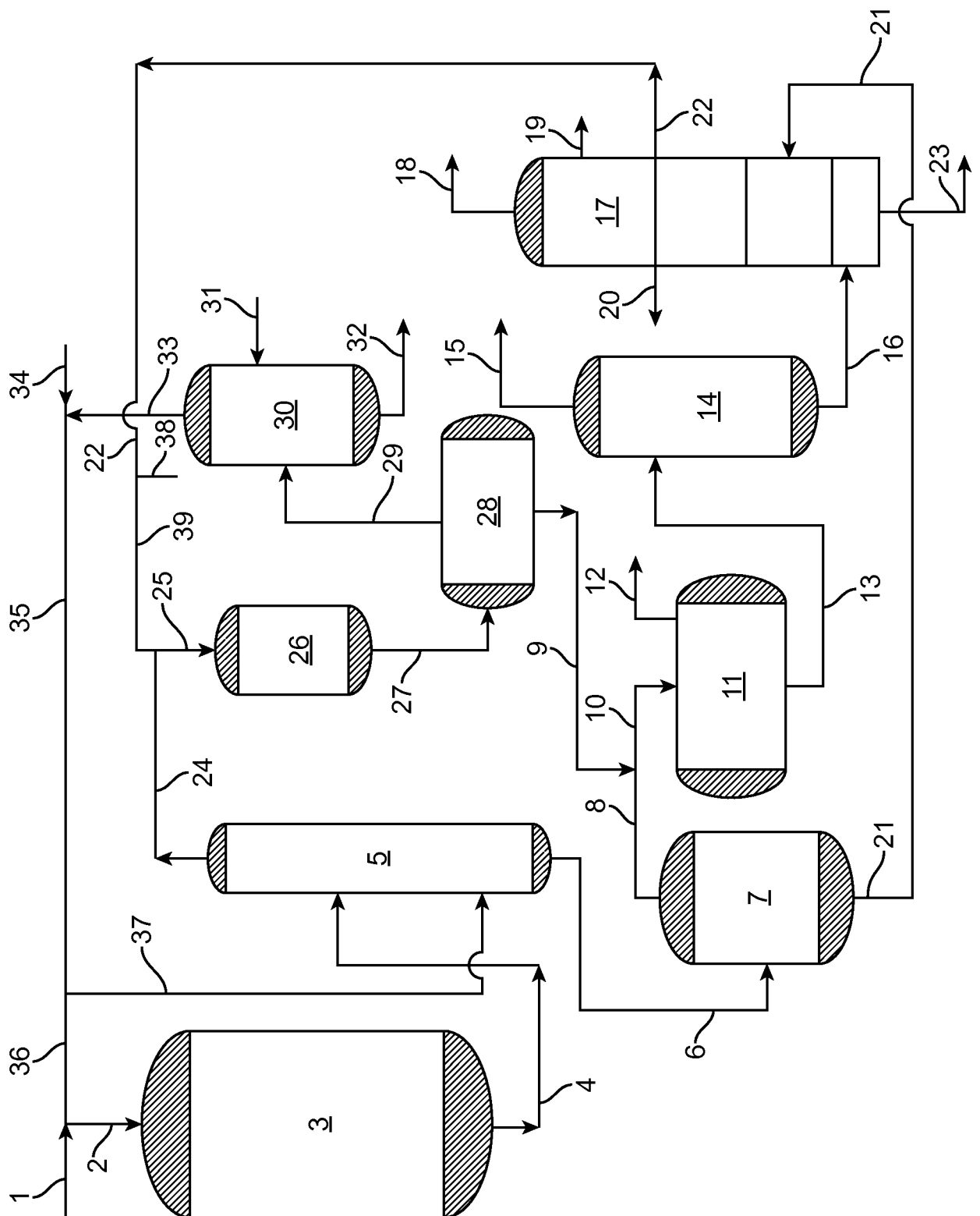
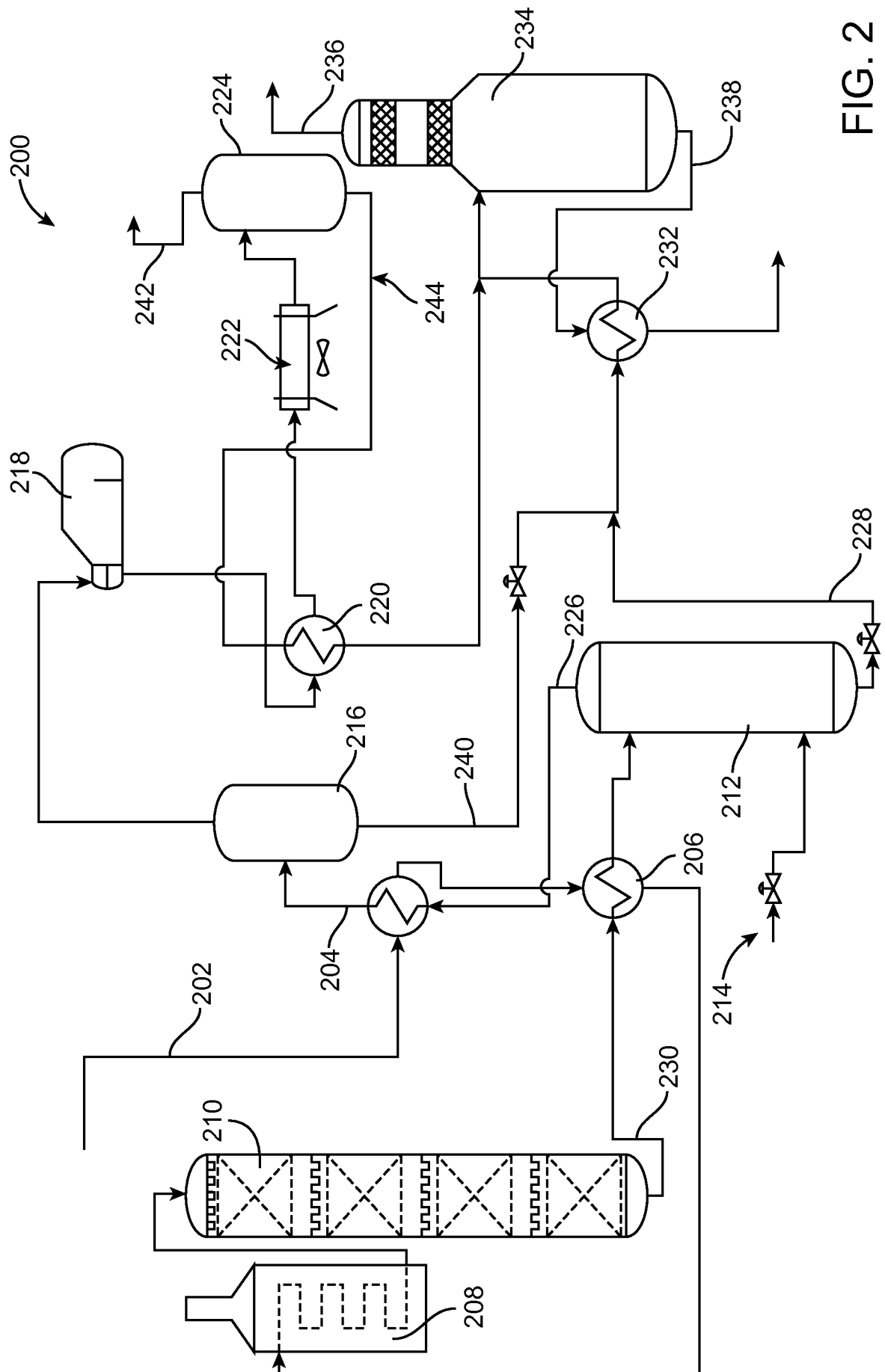


FIG. 1



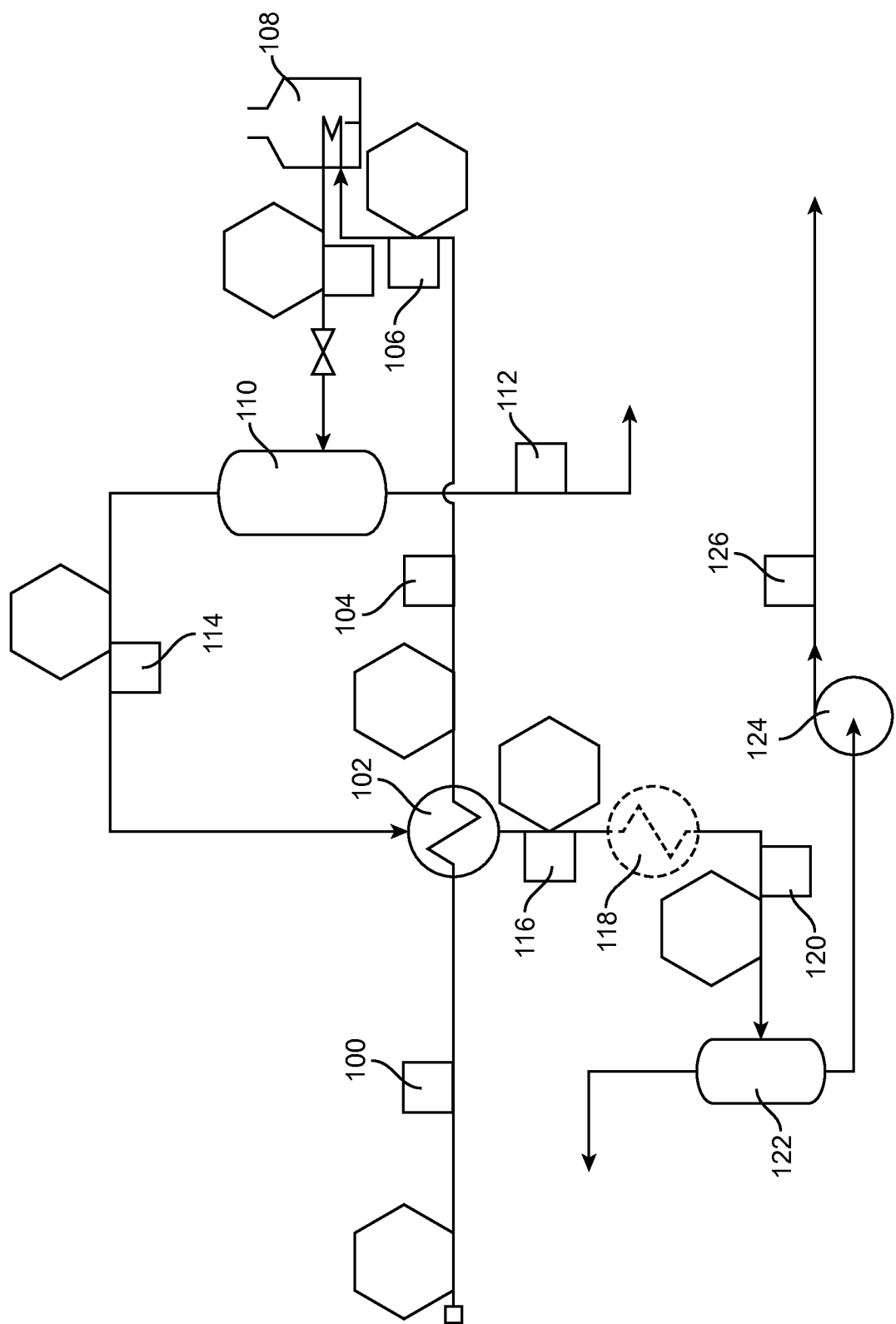


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/041643

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G47/00 C10G55/04
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)

EPO-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 2009/200201 A1 (CHEN CONG-YAN [US]) 13 August 2009 (2009-08-13)	1-17
Y	see paragraph [0003], line 11="NiMo/Alumina"; see page 3 C Hydrotreating catalyst; D Hydrofinishing catalyst. see table 3; Ni-Mo and Pt-Pd example 3 products; and comparative example 1 Ni-Mo products; see table 4; see paragraph [0077] of example 3. ----- -/--	1-17



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

21 August 2012

Date of mailing of the international search report

26/09/2012

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PCT/US2012/041643

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/052017 A2 (UOP LLC [US]; KOKAYEFF PETER [US]; DZIABALA BART [US]; LEONARD LAURA E) 23 April 2009 (2009-04-23)	1-17
Y	see paragraphs [0023]-[0034] see paragraph [0035], line 2; see claims 1-10; see claim 9 separation zone 116,216.	1-17
X	----- IFP / GROUP TECHNOLOGIES: "REFINING PROCESSES 2004", HYDROCARBON PROCESSES 31 December 2004 (2004-12-31), pages HDC-HDT, XP002682101, Retrieved from the Internet: URL: http://www.aimsgt.com/technicalpapers/RefiningProcesses_2004.pdf	1-16
Y	SEE FIGURES OF HYDROCRACKING (1); HYDROCRACKING (2); HYDROCRACKING (3); HYDROCRACKING (4); HYDROCRACKING, RESID; HYDROCRACKING (5); HYDRODEAROMATIZATION; HYDROCRACKING/HYDROTREATING VGO/DAO;HYDRODESULFURIZATION; HYDRODESUFURIZATION-UDHDS; HYDROFINISHING/HYDROTREATING; HYDROFINISHING; HYDROTREATING (1); HYDROTREATING (2);HYDROTREATING (3); HYDROTREATING (4); -----	1-17
X	EP 1 149 886 A2 (UOP LLC [US]) 31 October 2001 (2001-10-31)	1-16
Y	see examples 1,2; see claims 1-10; see figures 1-2. see [0030] -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/041643

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009200201	A1	13-08-2009	NONE

WO 2009052017	A2	23-04-2009	CA 2702395 A1 23-04-2009
		CN 101896579 A	24-11-2010
		EP 2201087 A2	30-06-2010
		RU 2010119514 A	27-11-2011
		US 2009095655 A1	16-04-2009
		WO 2009052017 A2	23-04-2009

EP 1149886	A2	31-10-2001	AT 277148 T 15-10-2004
		CA 2344953 A1	25-10-2001
		DE 60105688 D1	28-10-2004
		DE 60105688 T2	06-10-2005
		EP 1149886 A2	31-10-2001
		ES 2225338 T3	16-03-2005
		US 6379535 B1	30-04-2002
		US 6858128 B1	22-02-2005
