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14/524,301 27 October 2014 (27.10.2014) US(71) Applicant: UOP LLC [US/US]; 25 East Algonquin Road,
P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) Inventors: TSAI, Robert Edison; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US). ZHU, Xin X.; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US). GLOVER, Bryan K.; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US). ADAMOPOULOS, Eleftherios; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US). YANEZ, William; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) Agent: ROMANO, Ashley E.; UOP LLC, 25 East Algonquin Road, P.O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

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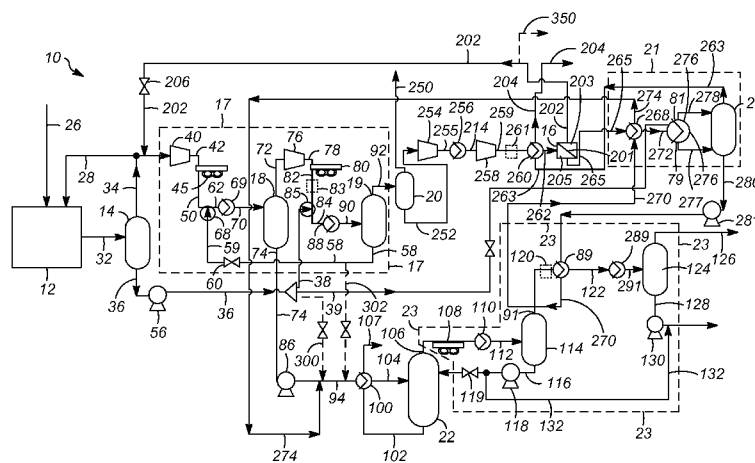


FIG. 1

(57) Abstract: Embodiments of apparatuses and methods for reforming of hydrocarbons including recovery of products are provided. In one example, a method comprises separating a reforming-zone effluent into a net gas phase stream and a liquid phase hydrocarbon stream. The net gas phase stream is separated for forming an H₂-rich stream and a first intermediate liquid phase hydrocarbon stream. The H₂-rich stream is contacted with an adsorbent to form an H₂-ultra rich stream and a PSA tail gas stream. The PSA tail gas stream is contacted with an H₂/hydrocarbon separation membrane to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon containing non-permeate residue stream.

METHODS AND APPARATUSES FOR REFORMING OF HYDROCARBONS
INCLUDING RECOVERY OF PRODUCTS USING A RECOVERY ZONE, A
PRESSURE SWING ADSORPTION ZONE, AND A MEMBRANE SEPARATION
ZONE

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STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 14/524,301 which was filed October 27, 2014, the contents of which are hereby incorporated by reference in its entirety.

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TECHNICAL FIELD

[0002] The technical field relates generally to reforming of hydrocarbons, and more particularly relates to apparatuses and methods for reforming of hydrocarbons with improved recovery of products from a reforming-zone effluent.

BACKGROUND

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[0003] High octane gasoline is needed for modern gasoline engines. Previously, octane numbers were often improved by incorporating various lead-containing additives into the gasoline. As lead-containing additives have been phased out of gasoline for environmental reasons, it has become increasingly necessary to rearrange the structure of the hydrocarbons used in gasoline blending to achieve higher octane ratings. Catalytic reforming of hydrocarbons is a process widely used by refiners for upgrading the octane ratings of gasoline as well as for other useful hydrocarbon conversion applications.

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[0004] In catalytic reforming, a hydrocarbon feedstock of, for example, C₅ hydrocarbons to C₁₁ hydrocarbons, is contacted with a reforming catalyst to convert at least a portion of the heavier hydrocarbons to aromatic hydrocarbons, for example, to increase the octane content of gasoline. The catalytic reforming of the heavier hydrocarbons to produce a reformate that includes aromatic hydrocarbons also produces significant quantities of valuable hydrogen and lighter hydrocarbons, such as liquefied petroleum gas (LPG) containing primarily C₃ and C₄ hydrocarbons. Refiners are looking for ways to maximize the recovery of reforming products, such as reformate, hydrogen and LPG, from the reforming reactor effluent.

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[0005] Accordingly, it is desirable to provide apparatuses and methods for reforming of hydrocarbons with improved recovery of products from a reforming reactor effluent.

Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.

BRIEF SUMMARY

5 [0006] Apparatuses and methods for reforming of hydrocarbons including recovery of products are provided herein. In accordance with an exemplary embodiment, an apparatus for reforming of hydrocarbons including recovery of products comprises a separation zone. The separation zone is configured to receive and separate a reforming-zone effluent that comprises H_2 , C_4^- hydrocarbons, and C_5^+ hydrocarbons including aromatics to form a
10 net gas phase stream that comprises H_2 and C_6^- hydrocarbons and a liquid phase hydrocarbon stream that comprises C_5^+ hydrocarbons. A recovery zone is configured to receive and separate the net gas phase stream for forming an H_2 -rich stream and a first intermediate liquid phase hydrocarbon stream. The first intermediate liquid phase hydrocarbon stream is enriched with C_3/C_4 hydrocarbons and further comprises C_5^+
15 hydrocarbons. A pressure swing adsorption (PSA) zone contains an adsorbent for selectively separating H_2 from hydrocarbons. The PSA zone is configured for receiving the H_2 -rich stream and for contacting the H_2 -rich stream with the adsorbent to form an H_2 -ultra rich stream and a PSA tail gas stream that comprises H_2 , C_2^- hydrocarbons, and some C_3^+ hydrocarbons. A membrane separation zone comprises an H_2 /hydrocarbon separation
20 membrane and is configured for receiving the PSA tail gas stream and for contacting the PSA tail gas stream with the H_2 /hydrocarbon separation membrane to form an H_2 -ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream.

[0007] In accordance with another exemplary embodiment, a method for reforming of
25 hydrocarbons including recovery of products is provided. The method comprises the steps of separating a reforming-zone effluent that comprises H_2 , C_4^- hydrocarbons, and C_5^+ hydrocarbons including aromatics to form a net gas phase stream that comprises H_2 and C_6^- hydrocarbons and a liquid phase hydrocarbon stream that comprises C_5^+ hydrocarbons. The net gas phase stream is separated for forming an H_2 -rich stream and a first
30 intermediate liquid phase hydrocarbon stream. The first intermediate liquid phase hydrocarbon stream is enriched with C_3/C_4 hydrocarbons and further comprises C_5^+ hydrocarbons. The H_2 -rich stream is contacted with an adsorbent that selectively separates

H₂ from hydrocarbons to form an H₂-ultra rich stream and a pressure swing adsorption (PSA) tail gas stream that comprises H₂, C₂⁻ hydrocarbons, and some C₃⁺ hydrocarbons. The PSA tail gas stream is contacted with an H₂/hydrocarbon separation membrane to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream.

[0008] In accordance with another exemplary embodiment, a method for reforming of hydrocarbons including recovery of products is provided. The method comprises the steps of combining a gas phase stream that comprises H₂ and C₆⁻ hydrocarbons with a liquid phase hydrocarbon stream that comprises C₅⁺ hydrocarbons including aromatics to extract C₃/C₄ hydrocarbons from the gas phase stream to the liquid phase hydrocarbon stream to form an H₂-rich stream that comprises primarily H₂ and an intermediate liquid phase hydrocarbon stream that is enriched with C₃/C₄ hydrocarbons and further comprises C₅⁺ hydrocarbons. The H₂-rich stream is contacted with an adsorbent that selectively separates H₂ from hydrocarbons and that is contained in a pressure swing adsorption (PSA) zone to form an H₂-ultra rich stream and a PSA tail gas stream that comprises H₂, C₂⁻ hydrocarbons, and some C₃⁺ hydrocarbons. The PSA tail gas stream is contacted with an H₂/hydrocarbon separation membrane to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream. The intermediate liquid phase hydrocarbon stream is separated in a stabilizer to form a C₅⁺ hydrocarbon-rich reformat stream that comprises primarily C₅⁺ hydrocarbons and a stabilizer gas stream that comprises H₂ and C₄⁻ hydrocarbons. At least a portion of the stabilizer gas stream is partially condensed and cooled to form a partially condensed stabilizer net gas stream. The partially condensed stabilizer net gas stream is separated in a separator to form a C₃/C₄ hydrocarbon-rich LPG stream that comprises primarily C₃/C₄ hydrocarbons and a light ends gas stream that comprises H₂ and C₂⁻ hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The various embodiments will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

[0010] FIG. 1 schematically illustrates an apparatus and a method for reforming of hydrocarbons including recovery of products in accordance with an exemplary embodiment; and

[0011] FIG. 2 schematically illustrates an apparatus and a method for reforming of hydrocarbons including recovery of products in accordance with another exemplary embodiment.

DETAILED DESCRIPTION

5 [0012] The following Detailed Description is merely exemplary in nature and is not intended to limit the various embodiments or the application and uses thereof. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

10 [0013] Various embodiments contemplated herein relate to apparatuses and methods for reforming of hydrocarbons with improved recovery of products from a reforming-zone effluent. The exemplary embodiments taught herein provide a separation zone in fluid communication with a reforming zone to receive a reforming-zone effluent. As used herein, the term “zone” refers to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor
15 vessels, scrubbers, strippers, fractionators or distillation columns, absorbers or absorber vessels, regenerators, heaters, exchangers, coolers/chillers, pipes, pumps, compressors, controllers, and the like. Additionally, an equipment item can further include one or more zones or sub-zones. The reforming-zone effluent comprises hydrogen (H_2), C_4^- hydrocarbons, and C_5^+ hydrocarbons including aromatics. As used herein, C_x means
20 hydrocarbon molecules that have “X” number of carbon atoms, C_x^+ means hydrocarbon molecules that have “X” and/or more than “X” number of carbon atoms, and C_x^- means hydrocarbon molecules that have “X” and/or less than “X” number of carbon atoms.

[0014] The separation zone separates the reforming-zone effluent to form a net gas phase stream and a liquid phase hydrocarbon stream. The net gas phase stream comprises
25 H_2 and C_6^- hydrocarbons and the liquid phase hydrocarbon stream comprises C_5^+ hydrocarbons. In a recovery zone, the net gas phase stream is separated to form an H_2 -rich stream and a first intermediate liquid phase hydrocarbon stream. In one example, in the recovery zone, the net gas phase stream and a first portion of the liquid phase hydrocarbon stream are combined to extract C_3/C_4 hydrocarbons from the net gas phase stream to the
30 first portion of the liquid phase hydrocarbon stream and to form a first two-phase combined stream. In an exemplary embodiment, the first two-phase combined stream is partially cooled and separated into the H_2 -rich stream and the first intermediate liquid

phase hydrocarbon stream. The first intermediate liquid phase hydrocarbon stream is enriched with C_3/C_4 hydrocarbons and further comprises C_5^+ hydrocarbons including aromatics. As used herein, the term “rich” means the corresponding component(s) is present in an amount of 70 mole percent (mole %) or greater, such as 80 mole % or greater. As used herein, the term “enriched” means that the concentration of the corresponding component(s) has increased relative to its original or previous concentration.

[0015] In an exemplary embodiment, the H_2 -rich stream is passed along to a pressure swing adsorption (PSA) zone that contains an adsorbent for selectively separating H_2 from hydrocarbons and impurities such as carbon monoxide and/or nitrogen. In the PSA zone, the H_2 -rich stream is contacted with the adsorbent to form an H_2 -ultra rich stream and a PSA tail gas stream that comprises H_2 , C_2^- hydrocarbons, and some C_3^+ hydrocarbons and impurities such as carbon monoxide and/or nitrogen. As used herein, the term “ultra rich” means 90 mole % or greater. As used herein, the term “some” means less than 50 mole %, such as 40 mole % or less, such as 30 mole % or less, such as 20 mole % or less, such as 10 mole % or less, for example from 10 to 0.01 mole %.

[0016] In a membrane separation zone, the PSA tail gas stream is contacted with the H_2 /hydrocarbon separation membrane for separating H_2 from hydrocarbons and to form an H_2 -ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream. In an exemplary embodiment, the H_2 /hydrocarbon separation membrane is a H_2 /hydrocarbon-CO- N_2 separation membrane and separates H_2 from hydrocarbons and carbon monoxide and nitrogen. The PSA tail gas hydrocarbon-containing non-permeate residue stream, which may also contain carbon monoxide and/or nitrogen, and at least a portion (e.g., a second portion) of the liquid phase hydrocarbon stream are passed along to an absorption zone and cooled to form a cooled PSA tail gas hydrocarbon-containing non-permeate residue stream and a cooled liquid phase hydrocarbon stream, respectively. In an exemplary embodiment, the absorption zone includes an absorber in which the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream is contacted with the cooled liquid phase hydrocarbon stream, for example, in countercurrent contacting flow, to extract C_3/C_4 hydrocarbons from the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream to the cooled liquid phase hydrocarbon stream to form a H_2 , C_2^- hydrocarbons-containing gas stream and a cooled second intermediate liquid phase

hydrocarbon stream. The cooled second intermediate liquid phase hydrocarbon stream is enriched with C_3/C_4 hydrocarbons and further comprises C_5^+ hydrocarbons including aromatics.

5 [0017] In an exemplary embodiment, the cooled second intermediate liquid phase hydrocarbon stream is passed through at least one heater and/or heat exchanger(s) to form a heated second intermediate liquid phase hydrocarbon stream. The heated second intermediate liquid phase hydrocarbon stream is separated in a stabilizer to form a C_5^+ hydrocarbon-rich reformat stream that comprises primarily C_5^+ hydrocarbons including aromatics and a stabilizer gas stream that comprises H_2 and C_4^- hydrocarbons. As used
10 herein, the term “primarily” means 50 mole % or greater. A stabilizer gas separation zone partially condenses, cools and further separates at least a portion of the stabilizer gas stream to form a C_3/C_4 hydrocarbon-rich LPG stream that comprises primarily C_3/C_4 hydrocarbons and a light ends gas stream that comprises H_2 and C_2^- hydrocarbons.

[0018] Referring to FIG. 1, an apparatus 10 for reforming of hydrocarbons in
15 accordance with an exemplary embodiment is provided. The apparatus 10 comprises a reforming zone 12, a separation zone 14, a recovery zone 17 including recontact drums 18 and 19, a pressure swing adsorption (PSA) zone 20, a membrane separation zone 16, an absorption zone 21 including an absorber 25 (e.g., multi-stage vessel or separation vessel that contains trays or packing), a stabilizer 22, and a stabilizer gas separation zone 23 that
20 are in fluid communication.

[0019] In an exemplary embodiment, a reforming-zone feedstock 26 containing naphtha fraction hydrocarbons, such as from C_5 to C_{11} hydrocarbons with a boiling point range of, for example, from 70 to 205°C, is introduced to the apparatus 10. The reforming-zone feedstock 26 and a recycle net gas phase stream 28 (discussed in further detail below) are
25 passed along to the reforming zone 12 that contains a reforming catalyst as is well-known in the art. The reforming zone 12 will typically comprise a plurality of stacked or side-by-side reactors with provisions for intermediate heating of the intermediate reactant stream (e.g., the reforming-zone feedstock 26 and the recycle net gas phase stream 28 including any conversion products formed therefrom) and one or more heat exchangers. In an
30 exemplary embodiment, in the reforming zone 12, the recycle net gas phase stream 28 is combined with the reforming-zone feedstock 26 for contact with the reforming catalyst.

[0020] A reforming-zone effluent 32 is formed in the reforming zone 12 and contains H_2 , C_5^+ hydrocarbons including aromatics, and lighter hydrocarbons such as C_4^- hydrocarbons including C_3 and C_4 hydrocarbons. In an exemplary embodiment, the reforming-zone effluent 32 is a two-phase liquid-gas stream in which H_2 and the lighter hydrocarbons (e.g., C_4^- hydrocarbons) are predominately in the gas phase and the heavier hydrocarbons (e.g., C_5^+ hydrocarbons including aromatics) are predominately in the liquid phase. In one embodiment, the reforming-zone effluent 32 has a temperature of from 35 to 50°C and, independently, a pressure of from 240 to 830 kPa gauge.

[0021] The reforming-zone effluent 32 is introduced to the separation zone 14. The separation zone 14 separates the reforming-zone effluent 32 into net gas phase stream 34 and a liquid phase hydrocarbon stream 36. In an exemplary embodiment, the net gas phase stream 34 comprises H_2 , C_6^- hydrocarbons, and impurities such as carbon monoxide and/or nitrogen, and the liquid phase hydrocarbon stream 36 comprises C_5^+ hydrocarbons including aromatics. In one example, the net gas phase stream 34 comprises H_2 present in an amount of from 80 to 90 mole %, C_1 hydrocarbons present in an amount of 2 to 5 mole %, C_2 hydrocarbons present in an amount of from 2 to 5 mole %, C_3 hydrocarbons present in an amount of from 2 to 4 mole %, C_4 hydrocarbons present in an amount of from 1.5 to 2.5 mole %, and possibly some C_5^+ hydrocarbons. In another example, the liquid phase hydrocarbon stream 36 comprises C_5^+ hydrocarbons present in an amount of from 90 to 99.9 mole % and possibly some C_4^- hydrocarbons and H_2 . In an exemplary embodiment, the separation zone 14 is operated at a temperature of from 35 to 50°C and, independently, a pressure of from 240 to 830 kPa gauge.

[0022] A portion of the net gas phase stream 34 is passed back to the reforming zone 12 as the recycle net gas phase stream 28 (as discussed above) and a remaining portion of the net gas phase stream 34 is passed along to the recovery zone 17 and introduced to a compressor 40. As illustrated and will be discussed in further detail below, in an exemplary embodiment, a H_2 -ultra rich permeate stream 202 is passed through a valve 206 and is introduced to the net gas phase stream 34 upstream from the compressor 40. Although not illustrated, alternatively the H_2 -ultra rich permeate stream 202 may be passed along to other locations in the recovery zone 17, such as, for example, stream 72, which is discussed in further detail below. The compressor 40 compresses the net gas phase stream 34, including the H_2 -ultra rich permeate stream 202, to form a compressed

net gas phase stream 42. In an exemplary embodiment, the compressed net gas phase stream 42 has a temperature of from 120 to 150°C and, independently, a pressure of from 720 to 2,490 kPa gauge.

5 **[0023]** The compressed net gas phase stream 42 is passed along to a cooler 45. In the cooler 45, the compressed net gas phase stream 42 is partially cooled to form a partially cooled, compressed net gas phase stream 50. In an exemplary embodiment, the partially cooled, compressed net gas phase stream 50 has a temperature of from 30 to 65°C and, independently, a pressure of from 690 to 2,460 kPa gauge.

10 **[0024]** In an exemplary embodiment, the liquid phase hydrocarbon stream 36 exits the separation zone 14 and is passed through a pump 56 and divided into portions 38 and 39, and optionally portion 300 discussed in further detail below. The recovery zone 17 may be configured as a countercurrent gas and liquid phase recovery zone for further separating H₂, C₃/C₄ hydrocarbons, and/or C₅⁺ hydrocarbons via extraction and/or absorption by contacting the liquid and gas phase fractions of the net gas phase stream 34 and the liquid
15 phase hydrocarbon stream 36. Alternatively, the recovery zone 17 is not limited to countercurrent flow and that other modes, such as co-current modes as are known in the art, may be used for the recovery zone 17.

20 **[0025]** In an exemplary embodiment, in the recovery zone 17, the portion 38 of the liquid phase hydrocarbon stream 36 is enriched with C₃/C₄ hydrocarbons from the partially cooled, compressed net gas phase stream 50 and is cooled, which is discussed in further detail below, to form an intermediate liquid phase hydrocarbon stream 58. In an exemplary embodiment, the intermediate liquid phase hydrocarbon stream 58 comprises C₃/C₄ hydrocarbons and is rich in C₅⁺ hydrocarbons. In an exemplary embodiment, the intermediate liquid phase hydrocarbon stream 58 is passed through a valve 60 to reduce
25 pressure and form an intermediate liquid phase hydrocarbon stream 59. In an exemplary embodiment, the intermediate liquid phase hydrocarbon stream 59 has a temperature of from 4 to 50°C and, independently, a pressure of from 690 to 2,460 kPa gauge.

30 **[0026]** The intermediate liquid phase hydrocarbon stream 59 is introduced to the partially cooled, compressed net gas phase stream 50 to form a two-phase combined stream 62. Optionally, the recovery zone 17 includes a mixing device 68 that mixes the intermediate liquid phase hydrocarbon stream 59 with the partially cooled, compressed net gas phase stream 50 to form the two-phase combined stream 62. In an exemplary

embodiment, the mixing device 68 aggressively mixes or homogenizes the partially cooled, compressed net gas phase stream 50 into the intermediate liquid phase hydrocarbon stream 59 such that the gas phase is broken up into a plurality of small bubbles that are well dispersed in turbulent flow with a C_5^+ hydrocarbon-rich liquid phase so that C_3/C_4 hydrocarbons are readily extracted from the gas phase to the C_5^+ hydrocarbon-rich liquid phase. As such, the two-phase combined stream 62 has a gas phase that is rich in H_2 and substantially depleted of C_3^+ hydrocarbons and a liquid phase that is rich in C_3^+ hydrocarbons.

[0027] The mixing device 68 may be a static mixer, a jet mixer, or the like. In an exemplary embodiment, the mixing device 68 is a jet mixer and the intermediate liquid phase hydrocarbon stream 59 is a motive liquid at a higher pressure than the partially cooled, compressed net gas phase stream 50 such that the motive liquid moves rapidly through the jet mixer causing the partially cooled, compressed net gas phase stream 50 to be sucked into the jet mixer by a “Venturi effect,” such as occurs in an eductor or ejector, as a suction fluid to homogenize the partially cooled, compressed net gas phase stream 50 in the intermediate liquid phase hydrocarbon stream 59.

[0028] As illustrated, the two-phase combined stream 62 is passed through a cooler 69 to form a partially cooled two-phase combined stream 70. In an exemplary embodiment, the partially cooled two-phase combined stream 70 has a temperature of from 20 to 50°C and, independently, a pressure of from 660 to 2,430 kPa gauge.

[0029] The partially cooled two-phase combined stream 70 is introduced to the recontact drum 18. While the recovery zone 17 is illustrated as only having 2 recontact drums 18 and 19, it is to be understood that the recovery zone 17 can have more than 2 recontact drums or only a single recontact drum. The partially cooled two-phase combined stream 70 is separated in the recontact drum 18 into its corresponding gas and liquid phases to form an intermediate gas phase stream 72 that comprises H_2 and C_6^- hydrocarbons and an intermediate liquid phase hydrocarbon stream 74 that comprises C_3^+ hydrocarbons. In an exemplary embodiment, the intermediate gas phase stream 72 and, independently, the intermediate liquid phase hydrocarbon stream 74 each have a temperature of from 20 to 50°C and, independently, a pressure of from 660 to 2,430 kPa gauge.

[0030] The intermediate gas phase stream 72 exits the recontact drum 18 and is passed along to a compressor 76. The compressor 76 compresses the intermediate gas phase

stream 72 to form a compressed intermediate gas phase stream 78. In an exemplary embodiment, the compressed intermediate gas phase stream 78 has a temperature of from 120 to 160°C and, independently, a pressure of from 1,980 to 5,580 kPa gauge.

5 [0031] The compressed intermediate gas phase stream 78 is introduced to a cooler 80 to form a partially cooled, compressed intermediate gas phase stream 82. In an exemplary embodiment, the partially cooled, compressed intermediate gas phase stream 82 has a temperature of from 30 to 65°C and, independently, a pressure of from 1,950 to 5,550 kPa gauge.

10 [0032] The partially cooled, compressed intermediate gas phase stream 82 exits the cooler 80 and optionally, is passed through a dryer 83 (e.g., vessel with adsorbent material or the like adsorbing water or otherwise removing water) for removing water from the partially cooled, compressed intermediate gas phase stream 82 to help avoid the formation of hydrates. In an exemplary embodiment, upstream from the dryer 83, the partially cooled, compressed intermediate gas phase stream 82 includes water present in an amount
15 of 15 ppm by weight or greater, and after being passed through the dryer 83, the partially cooled, compressed intermediate gas phase stream 82 includes water present in an amount of less than 15 ppm by weight.

[0033] Next, the partially cooled, compressed intermediate gas phase stream 82 is combined with the portion 38 of the liquid phase hydrocarbon stream 36 to form an
20 intermediate two-phase combined stream 84. Optionally, in an exemplary embodiment, the apparatus 10 comprises a mixing device 85 (e.g., similarly configured to the mixing device 68 as discussed above) for aggressively mixing or homogenizing the partially cooled, compressed intermediate gas phase stream 82 into the portion 38 of the liquid phase hydrocarbon stream 36. As such, the partially cooled, compressed intermediate gas
25 phase stream 82 is broken up into a plurality of small bubbles that are well dispersed in turbulent flow with a C_5^+ hydrocarbon-rich liquid phase of the portion 38 of the liquid phase hydrocarbon stream 36 so that C_3/C_4 hydrocarbons are readily extracted from the gas phase to the C_5^+ hydrocarbon-rich liquid phase. In an exemplary embodiment, the intermediate two-phase combined stream 84 has a gas phase that is rich in H_2 and
30 substantially depleted of C_3^+ hydrocarbons and a liquid phase that is rich in C_3^+ hydrocarbons.

[0034] The intermediate two-phase combined stream 84 is passed along and introduced to a cooler 88. The cooler 88 partially cools the intermediate two-phase combined stream 84 to form a partially cooled intermediate two-phase combined stream 90. In an exemplary embodiment, the partially cooled intermediate two-phase combined stream 90 has a temperature of from 4 to 50°C and, independently, a pressure of from 1,920 to 5,520 kPa gauge.

[0035] The partially cooled intermediate two-phase combined stream 90 is introduced to the recontact drum 19. The partially cooled intermediate two-phase combined stream 90 is separated in the recontact drum 19 into its corresponding gas and liquid phases to form an H₂-rich stream 92 that comprises primarily H₂ and the intermediate liquid phase hydrocarbon stream 58 as discussed above. In an exemplary embodiment, the H₂-rich stream 92 and, independently, the intermediate liquid phase hydrocarbon stream 58 each have a temperature of from 4 to 50°C and, independently, a pressure of from 1,920 to 5,520 kPa gauge. In an exemplary embodiment, the H₂-rich stream 92 comprises H₂ present in an amount of from 80 to 95 mole % with some C₄⁻ hydrocarbons and impurities such as carbon monoxide and/or nitrogen.

[0036] The H₂-rich stream 92 is introduced to the PSA zone 20 for further purifying the stream 92 by removing hydrocarbons to form an H₂-ultra rich stream 250. In an exemplary embodiment, the PSA zone 20 contains an adsorbent (e.g., adsorbent material(s)) and is configured for contacting the H₂-rich stream 92 with the adsorbent for selectively separating H₂ from hydrocarbons (e.g., C₄⁻ hydrocarbons) and impurities such as carbon monoxide and/or nitrogen to form the H₂-ultra rich stream 250. The exemplary PSA zone 20 operates on the principle of selectively adsorbing hydrocarbons and/or other impurities (e.g., carbon monoxide and/or nitrogen) onto the adsorbent at a relatively high pressure (e.g., 1,920 to 5,520 kPa gauge) to form the H₂-ultra rich stream 250, and desorbing the hydrocarbons from the adsorbent at relatively low pressure (e.g., 10 to 500 kPa gauge) to regenerate the adsorbent and to form a PSA tail gas stream 252 that contains the hydrocarbons and/or other impurities (e.g., carbon monoxide and/or nitrogen).

[0037] In an exemplary embodiment, the PSA zone 20 includes a plurality of fixed-bed adsorption units each containing layers of different adsorbent materials where the lower layer or layers are filled with weaker adsorbent materials, e.g., relatively low affinity for adsorbing gaseous hydrocarbons, and the upper layer or layers are filled with stronger

adsorbent materials, e.g., relatively high affinity for adsorbing gaseous hydrocarbons (e.g., gaseous C_3^- hydrocarbons) and impurities (e.g., carbon monoxide and/or nitrogen). For example, the lower layer(s) can contain weakly adsorbent materials, such as activated alumina and/or silica gel, while the intermediate layer(s) can contain intermediate strength adsorbent materials, such as activated carbon, and the upper layer(s) can contain strong adsorbent materials, such as zeolite and/or molecular sieve materials. In an exemplary embodiment, the multiple fixed-bed adsorption units cooperatively operate in a staggered sequence to produce constant feed (e.g., the H_2 -rich stream 92), product (e.g., the H_2 -ultra rich stream 250), and tail gas (e.g., the PSA tail gas stream 252) flows. In an exemplary embodiment, the PSA zone 20 operates following a five-step pressure-swing cycle including an adsorption step, a co-current depressurization step, a counter-current depressurization step, a purge step, and a repressurization step. During the adsorption step, the H_2 -rich stream 92 enters a lower portion of the fixed-bed adsorption unit at a relatively high pressure, and as the feed gas rises in the unit, the hydrocarbons and impurities (e.g., carbon monoxide and/or nitrogen) are adsorbed in the various layers of the adsorbent materials depending upon their respective adsorption selectivity to form the H_2 -ultra rich stream 250. The co-current depressurization, counter-current depressurization and purge steps decrease the pressure in the fixed-bed adsorption unit and purge the unit with high purity gas from the product (e.g., the H_2 -ultra rich stream 250) or co-current depressurization steps, respectively, to remove the hydrocarbons and impurities (e.g., carbon monoxide and/or nitrogen) and regenerate the adsorption materials. The repressurization step increases the pressure in the fixed-bed adsorption unit with either feed gas (e.g., the H_2 -rich stream 92) or product gas (e.g., the H_2 -ultra rich stream 250) in preparation for the next adsorption step. Other pressure swing adsorption configurations for forming an H_2 -ultra rich stream known to those skilled in the art may also be used.

[0038] In an exemplary embodiment, the H_2 -ultra rich stream 250 comprises H_2 present in an amount of from 90 to less than 100 mole %, such as from 90 to 99.999 mole %, such as from 95 to 99.999 mole %, such as from 98 to 99.999 mole %, such as from 99 to 99.999 mole %, for example 99.99 mole %, and possibly some C_2^- hydrocarbons and impurities (e.g., carbon monoxide and/or nitrogen). In an exemplary embodiment, the H_2 -rich stream 250 has a temperature of from 30 to 50°C and, independently, a pressure of from 1,880 to 5,480 kPa gauge, for example 2,070 to 2,410 kPa gauge. In an exemplary

embodiment, the PSA tail gas stream 252 comprises C_2 - hydrocarbons present in an amount of from 25 to 80 mole %, H_2 present in an amount of from 25 to 75 mole %, and possibly some C_3^+ hydrocarbons and impurities (e.g., carbon monoxide and/or nitrogen). In an exemplary embodiment, the PSA tail gas stream 252 has a temperature of from 30 to 50°C and, independently, a pressure of from 10 to 500 kPa gauge, for example 20 to 50 kPa gauge.

[0039] The H_2 -ultra rich stream 250 is removed from the apparatus 10, for example, to be used as a hydrogen product stream. The PSA tail gas stream 252 is passed through a compressor 254 to form a compressed PSA tail gas stream 255 that is further advanced through a cooler 256 to partially cool the stream 255 and form a partially cooled, compressed PSA tail gas stream 214. In an exemplary embodiment, the partially cooled, compressed PSA tail gas stream 214 has a temperature of from 30 to 60°C and, independently, a pressure of from 690 to 3,000 kPa gauge, for example of from 690 to 800 kPa gauge.

[0040] As illustrated, the partially cooled, compressed PSA tail gas stream 214 is passed through a compressor 258 to form a partially cooled, further compressed PSA tail gas stream 259. In an exemplary embodiment, optionally, the partially cooled, further compressed PSA tail gas stream 259 is passed through a dryer 261 for removing water from the partially cooled, further compressed PSA tail gas stream 259 to help avoid the formation of hydrates. In an exemplary embodiment, upstream from the dryer 261, the partially cooled, further compressed PSA tail gas stream 259 includes water present in an amount of 15 ppm by weight or greater, and after being passed through the dryer 261, the partially cooled, further compressed PSA tail gas stream 259 includes water present in an amount of less than 15 ppm by weight.

[0041] Next, the partially cooled, further compressed PSA tail gas stream 259 is passed through a PSA tail gas heat exchanger 260 for indirect heat exchange with an H_2 , C_2^- hydrocarbons-containing gas stream 263, which is discussed in further detail below and may also contain impurities (e.g., carbon monoxide and/or nitrogen), to form a further partially cooled, further compressed PSA tail gas stream 262 and a partially heated H_2 , C_2^- hydrocarbons-containing gas stream 204. In an exemplary embodiment, the further partially cooled, further compressed PSA tail gas stream 262 has a temperature of from 30 to 150°C and, independently, a pressure of from 1,850 to 3,000 kPa gauge. In an

exemplary embodiment, the partially heated H_2 , C_2^- hydrocarbons-containing gas stream 204 has a temperature of from -12 to $85^\circ C$ and, independently, a pressure of from 500 to 2,690 kPa gauge. As illustrated, the partially heated H_2 , C_2^- hydrocarbons-containing gas stream 204 is removed from the apparatus 10, for example, to be used as fuel gas.

5 [0042] In an exemplary embodiment, the further partially cooled, further compressed PSA tail gas stream 262 is introduced to the membrane separation zone 16 for separation. The membrane separation zone 16 comprises an H_2 /hydrocarbon separation membrane 201 that is selectively permeable to H_2 while being effectively non-permeable to hydrocarbons, e.g., C_4^- hydrocarbons and impurities (e.g., carbon monoxide and/or
10 nitrogen). In commercially available embodiments, the H_2 /hydrocarbon separation membrane 201 may be in the form of either spiral wound or hollow fibers, made of cellulose acetate, cellulose triacetate, polyimide, polysulfone material or any other suitable material. Such fibers may be assembled into compact bundles to provide a large membrane area available for the passage of the desired product gas (H_2) therethrough.
15 Alternatively, the H_2 /hydrocarbon separation membrane 201 can be any other separation membrane known to those skilled in the art for separating H_2 , hydrocarbons, and impurities (e.g., carbon monoxide and/or nitrogen). In an exemplary embodiment, the H_2 /hydrocarbon separation membrane 201 has a selectivity of at least 60, preferably at least 75, for example from 75 to 370 or greater, of H_2 over C_4^- hydrocarbons, and other
20 impurities such as CO, N_2 and the like.

[0043] In an exemplary embodiment, the further partially cooled, further compressed PSA tail gas stream 262 enters the membrane separation zone 16 and H_2 in the stream 262 selectively permeates the H_2 /hydrocarbon separation membrane 201 to a permeate side 203 of the membrane 201 while the non-permeate hydrocarbon gas is withdrawn from a
25 non-permeate residue side 205 of the membrane 201. In an exemplary embodiment, H_2 is removed from the membrane separation zone 16 from the permeate side 203 to form the H_2 -ultra rich permeate stream 202 and the non-permeate hydrocarbon gas is removed from the membrane separation zone 16 from the non-permeate residue side 205 to form a PSA tail gas hydrocarbon-containing non-permeate residue stream 265, which also contains
30 impurities (e.g., carbon monoxide and/or nitrogen). Optionally, at least a portion of the H_2 -ultra rich permeate stream 202 may be removed from the apparatus 10 via line 350.

[0044] The PSA tail gas hydrocarbon-containing non-permeate residue stream 265 is introduced to the absorption zone 21. Likewise, the portion 39 of the liquid phase hydrocarbon stream is introduced to the absorption zone 21. In an exemplary embodiment, the absorption zone 21 is configured as a countercurrent gas and liquid phase absorption zone for further separating H₂, C₃/C₄ hydrocarbons, and/or C₅⁺ hydrocarbons via extraction and/or absorption by contacting the PSA tail gas hydrocarbon-containing non-permeate residue stream 265 and the portion 39 of the liquid phase hydrocarbon stream 36. As illustrated, in an exemplary embodiment, the absorption zone 21 comprises a single absorber 25 as well as other types of equipment items as will be described in further detail below. Alternatively, the absorption zone 21 may have more than one absorber as well as other types of equipment items.

[0045] The PSA tail gas hydrocarbon-containing non-permeate residue stream 265 is passed along to an absorption zone heat exchanger 268 for indirect heat exchange with a partially heated, second intermediate liquid phase hydrocarbon stream 270 to form a partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 272 and a partially heated, second intermediate liquid phase hydrocarbon stream 274. In an exemplary embodiment, the partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 272 has a temperature of from 20 to 45°C and, independently, a pressure of from 640 to 2,940 kPa gauge. In an exemplary embodiment, the partially heated, second intermediate liquid phase hydrocarbon stream 274 has a temperature of from 30 to 150°C and, independently, a pressure of from 1,000 to 1,500 kPa gauge.

[0046] The partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 272 is passed along to a dual-bundle chiller 276 that has a chiller section 79 and a chiller section 81 each configured for cooling. Alternatively, chiller sections 79 and 81 may be corresponding chiller sections in separate chillers. The partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 272 is passed through the chiller section 79 to further cool the stream 272 and form a cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277. In an exemplary embodiment, the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277 has a temperature of from -28 to 4°C, independently, a pressure of from 580 to 2,880 kPa gauge.

[0047] As illustrated, the portion 39 of the liquid phase hydrocarbon stream 36 is introduced to the dual-bundle chiller 276. The portion 39 of the liquid phase hydrocarbon

stream 36 is passed through the chiller section 81 to cool the portion 39 and form a cooled liquid phase hydrocarbon stream 278. In an exemplary embodiment, the cooled liquid phase hydrocarbon stream 278 has a temperature of from -28 to 4°C, and independently, a pressure of from 580 to 2,880 kPa gauge.

5 [0048] The cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277 and the cooled liquid phase hydrocarbon stream 278 are introduced to the absorber 25. As illustrated, in an exemplary embodiment, the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277 is introduced to a lower portion of the absorber 25 and rises upwardly while the cooled liquid phase hydrocarbon stream 278 is
10 introduced to an upper portion of the absorber 25 and descends downwardly for countercurrent contact with the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277. During contact in the absorber 25, C₃/C₄ hydrocarbons from the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream 277 are extracted and/or absorbed to the cooled liquid phase hydrocarbon stream 278 to form a
15 cooled second intermediate liquid phase hydrocarbon stream 280 that is enriched with C₃/C₄ hydrocarbons and further comprises C₅⁺ hydrocarbons and the H₂, C₂⁻ hydrocarbons-containing gas stream 263. In an exemplary embodiment, the cooled second intermediate liquid phase hydrocarbon stream 280 and, independently, the H₂, C₂⁻ hydrocarbons-containing gas stream 263 each have a temperature of from -28 to 4°C and,
20 independently, a pressure of from 580 to 2,880 kPa gauge.

[0049] In an exemplary embodiment, the cooled second intermediate liquid phase hydrocarbon stream 280 is optionally passed through a pump 281 and is introduced to the stabilizer gas separation zone 23. The cooled second intermediate liquid phase hydrocarbon stream 280 is passed through a stabilizer gas separation zone heat exchanger
25 89 for indirect heat exchange with a stabilizer net gas stream 91, which is discussed in further detail below, to form the partially heated, second intermediate liquid phase hydrocarbon stream 270. In an exemplary embodiment, the partially heated, second intermediate liquid phase hydrocarbon stream 270 has a temperature of from 15 to 65°C and, independently, a pressure of from 1,100 to 1,600 kPa gauge.

30 [0050] As discussed above, the partially heated, second intermediate liquid phase hydrocarbon stream 270 is passed through the absorption zone heat exchanger 268 to form the partially heated, second intermediate liquid phase hydrocarbon stream 274. The

intermediate liquid phase hydrocarbon stream 74 exits the recontact drum 18, is optionally passed through a pump 86, and is combined with the partially heated, second intermediate liquid phase hydrocarbon stream 274 to form a combined liquid phase hydrocarbon stream 94. Optionally, the combined liquid phase hydrocarbon stream 94 may also include a
5 corresponding portion(s) from the liquid phase hydrocarbon stream 36 and/or the intermediate liquid phase hydrocarbon stream 58 via line 300 and/or line 302, respectively. In an exemplary embodiment, the combined liquid phase hydrocarbon stream 94 has a temperature of from 20 to 150°C and, independently, a pressure of from 1,000 to 1,500 kPa gauge.

10 **[0051]** The combined liquid phase hydrocarbon stream 94 is passed through a stabilizer heat exchanger 100 for indirect heat exchange with a C_5^+ hydrocarbon-rich reformat stream 102, which is discussed in further detail below, to form a heated intermediate liquid phase hydrocarbon stream 104. In an exemplary embodiment, the heated intermediate liquid phase hydrocarbon stream 104 has a temperature of from 150 to 200°C and,
15 independently, a pressure of from 900 to 1,400 kPa gauge.

[0052] The heated intermediate liquid phase hydrocarbon stream 104 is passed along to the stabilizer 22. The stabilizer 22 separates the heated intermediate liquid phase hydrocarbon stream 104 into a stabilizer gas stream 106 that comprises H_2 and C_4^- hydrocarbons enriched with C_3/C_4 hydrocarbons and the C_5^+ hydrocarbon-rich reformat stream 102. In an exemplary embodiment, the C_5^+ hydrocarbon-rich reformat stream 102
20 comprises C_5^+ hydrocarbons including aromatics present in an amount of 90 to 99.9 mole %. As discussed above, the C_5^+ hydrocarbon-rich reformat stream 102 is passed through the stabilizer heat exchanger 100 and is removed from the apparatus 10 as a reformat product 107.

25 **[0053]** The stabilizer gas stream 106 is introduced to the stabilizer gas separation zone 23 and is passed through a first cooler 108 (e.g., an air cooler) and a second cooler 110 (e.g., a water cooler) to partially condense and cool the stream 106 and form a partially condensed stabilizer gas stream 112. In an exemplary embodiment, the partially condensed stabilizer gas stream 112 has a temperature of from 30 to 65°C and,
30 independently, a pressure of from 800 to 1,300 kPa gauge.

[0054] The partially condensed stabilizer gas stream 112 is passed along to a receiver 114 (e.g., stabilizer overhead receiver) to remove condensed/liquid hydrocarbons from the

stream 112 and to form the stabilizer net gas stream 91 as discussed above and a C_3^+ hydrocarbons-containing liquid phase stream 116. The C_3^+ hydrocarbons-containing liquid phase stream 116 exits the receiver 114 and is passed along through a pump 118 and a valve 119 back to the stabilizer 22 as a recycle stream.

5 [0055] The stabilizer net gas stream 91 is passed towards the stabilizer gas separation zone heat exchanger 89. Optionally, in an exemplary embodiment, the stabilizer gas separation zone 23 includes a dryer 120 upstream from the stabilizer gas separation zone heat exchanger 89 for removing water from the stabilizer net gas stream 91 to help avoid the formation of hydrates. In an exemplary embodiment, upstream from the dryer 120, the
10 stabilizer net gas stream 91 includes water present in an amount of 15 ppm by weight or greater, and after being passed through the dryer 120, the stabilizer net gas stream 91 includes water present in an amount of less than 15 ppm by weight.

[0056] As discussed above, the stabilizer net gas stream 91 is passed through the stabilizer gas separation zone heat exchanger 89 for indirect heat exchange with the cooled
15 second intermediate liquid phase hydrocarbon stream 280 to partially condense and cool the stream 91 and to form a partially condensed stabilizer net gas stream 122. Although the stabilizer net gas stream 91 is shown as being passed through only a single stabilizer gas separation zone heat exchanger 89, the stream 91 may be partially condensed and cooled by being advanced through one or more heat exchangers, chillers, coolers, or
20 combination thereof. In an exemplary embodiment, the partially condensed stabilizer net gas stream 122 has a temperature of from 10 to 25°C and, independently, a pressure of from 700 to 1,200 kPa gauge.

[0057] The partially condensed stabilizer net gas stream 122 is passed through a chiller 289 to further condense and cool the stream 122 and form a further partially condensed
25 stabilizer net gas stream 291. In an exemplary embodiment, the further partially condensed stabilizer net gas stream 291 has a temperature of from -28 to 4°C and, independently, a pressure of from 660 to 1,160 kPa gauge.

[0058] The further partially condensed stabilizer net gas stream 291 is introduced to a separator 124. The separator 124 may be configured as a flash drum, or alternatively, may
30 be configured as a multi-stage fractionation tower. The separator 124 separates C_3/C_4 hydrocarbons and any remaining H_2 and C_2^- hydrocarbons from the further partially condensed stabilizer net gas stream 291 to form a light ends gas stream 126 and a C_3/C_4

hydrocarbon-rich LPG stream 128. In an exemplary embodiment, the C₃/C₄ hydrocarbon-rich LPG stream 128 comprises C₃/C₄ hydrocarbons present in an amount of 70 to 99.9 mole % and the light ends gas stream 126 comprises H₂ present in an amount of from 0 to 20 mole %, C₂⁻ hydrocarbons present in an amount of from 20 to 95 mole %, and possibly some C₃⁺ hydrocarbons. As illustrated, the C₃/C₄ hydrocarbon-rich LPG stream 128 is passed through a pump 130, is optionally combined with a side stream 132 of the C₃⁺ hydrocarbons-containing liquid phase stream 116, and is removed from the apparatus 10 as an LPG product stream. The light ends gas stream 126 is removed from the apparatus 10 to be used, for example, as fuel gas.

[0059] Referring to FIG. 2, an apparatus 210 for reforming of hydrocarbons in accordance with another exemplary embodiment is provided. The apparatus 210 is similarly configured to the apparatus 10 including the reforming zone 12, the separation zone 14, the recovery zone 217 including knockout drums 218 and 219, the PSA zone 20, the membrane separation zone 16, the absorption zone 21 including the absorber 25, the stabilizer 22, and the stabilizer gas separation zone 23 as discussed above in relation to FIG. 1 with the exceptions that the liquid phase hydrocarbon stream 36 is advanced to the absorption zone 21 with zero flow or effectively zero flow to the recovery zone 217 and the intermediate liquid phase hydrocarbon stream 58 is combined with the intermediate liquid phase hydrocarbon stream 74 and the stream 274 to form the combined liquid phase hydrocarbon stream 94. Optionally, the combined liquid phase hydrocarbon stream 94 may also include a portion from the liquid phase hydrocarbon stream 36 via line 300.

[0060] With respect to the recovery zone 217, in particular, the partially cooled, compressed net gas phase stream 50 is passed through the cooler 69 to the knockout drum 218 to form intermediate gas phase stream 72 and the intermediate liquid phase hydrocarbon stream 74. Further downstream, the partially cooled, compressed intermediate gas phase stream 82 is passed through the cooler 88 and introduced to the knockout drum 219 to form the H₂-rich stream 92 and the intermediate liquid phase hydrocarbon stream 58.

[0061] Accordingly, apparatuses and methods for reforming of hydrocarbons with improved recovery of products from a reforming-zone effluent have been described. The exemplary embodiments taught herein separate the reforming-zone effluent in a separation zone to form a net gas phase stream and a liquid phase hydrocarbon stream. The net gas

phase stream is separated in a recovery zone for forming an H₂-rich stream and a first intermediate liquid phase hydrocarbon stream. The H₂-rich stream is contacted with an adsorbent in a pressure swing adsorption (PSA) zone to form an H₂-ultra rich stream and a PSA tail gas stream. The PSA tail gas stream is contacted with an H₂/hydrocarbon separation membrane in a membrane separation zone to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream. The PSA tail gas hydrocarbon-containing non-permeate residue stream and at least a portion of the liquid phase hydrocarbon stream are cooled and contacted in an absorption zone to form a H₂, C₂⁻ hydrocarbons-containing gas stream and a cooled second intermediate liquid phase hydrocarbon stream. The cooled second intermediate liquid phase hydrocarbon stream is further separated to form a C₅⁺ hydrocarbon-rich reformat stream, a light ends gas stream, and a C₃/C₄ hydrocarbon-rich LPG stream.

SPECIFIC EMBODIMENTS

[0062] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0063] A first embodiment of the invention is an apparatus for reforming of hydrocarbons including recovery of products, the apparatus comprising a separation zone configured to receive and separate a reforming-zone effluent that comprises H₂, C₄-hydrocarbons, and C₅⁺ hydrocarbons including aromatics to form a net gas phase stream that comprises H₂ and C₆- hydrocarbons and a liquid phase hydrocarbon stream that comprises C₅⁺ hydrocarbons including aromatics; a recovery zone configured to receive and separate the net gas phase stream for forming an H₂-rich stream and a first intermediate liquid phase hydrocarbon stream that is enriched with C₃/C₄ hydrocarbons and further comprises C₅⁺ hydrocarbons; a pressure swing adsorption (PSA) zone containing an adsorbent for selectively separating H₂ from hydrocarbons, wherein the PSA zone is configured for receiving the H₂-rich stream and for contacting the H₂-rich stream with the adsorbent to form an H₂-ultra rich stream and a PSA tail gas stream that comprises H₂, C₂⁻ hydrocarbons, and some C₃⁺ hydrocarbons; and a membrane separation zone comprising an H₂/hydrocarbon separation membrane and configured for receiving the PSA tail gas stream and for contacting the PSA tail gas stream with the

H₂/hydrocarbon separation membrane to form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the recovery zone is configured to receive the H₂-ultra rich permeate stream with the net gas phase stream for forming the H₂-rich stream and the first intermediate liquid phase hydrocarbon stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising an absorption zone configured to receive and cool the PSA tail gas hydrocarbon-containing non-permeate residue stream and at least a portion of the liquid phase hydrocarbon stream to form a cooled PSA tail gas hydrocarbon-containing non-permeate residue stream and a cooled liquid phase hydrocarbon stream, respectively, wherein the absorption zone comprises an absorber that is configured for contacting the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream with the cooled liquid phase hydrocarbon stream to extract C₃/C₄ hydrocarbons from the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream to the cooled liquid phase hydrocarbon stream to form a H₂, C₂-hydrocarbons-containing gas stream and a cooled second intermediate liquid phase hydrocarbon stream that is enriched with C₃/C₄ hydrocarbons. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising at least one compressor and at least one cooler, heat exchanger, or combinations thereof cooperatively configured to receive the PSA tail gas stream and to compress and partially cool the PSA tail gas stream to form a further partially cooled, further compressed PSA tail gas stream, and wherein the membrane separation zone is configured to receive the further partially cooled, further compressed PSA tail gas stream for contact with the H₂/hydrocarbon separation membrane to form the H₂-ultra rich permeate stream and the PSA tail gas hydrocarbon-containing non-permeate residue stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising a dryer that is cooperatively arranged with the at least one compressor and the at least one cooler, heat exchanger, or combinations thereof so as to remove water from the PSA tail gas stream before the further partially cooled, further compressed PSA tail gas stream is introduced to the membrane separation zone. An embodiment of the invention is one, any

or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the at least one compressor and the at least one cooler, heat exchanger, or combinations thereof are cooperatively configured to receive the PSA tail gas stream and to compress and partially cool the PSA tail gas stream to form a partially cooled, further compressed PSA tail gas stream, and wherein the at least one cooler, heat exchanger, or combinations thereof comprises a PSA tail gas heat exchanger that is configured for indirect heat exchange between the partially cooled, further compressed PSA tail gas stream and the H₂, C₂- hydrocarbons-containing gas stream to form the further partially cooled, further compressed PSA tail gas stream and a partially heated H₂, C₂- hydrocarbons-containing gas stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the absorption zone comprises at least one heat exchanger, first chiller section, or combinations thereof configured to receive and cool the PSA tail gas hydrocarbon-containing non-permeate residue stream to form the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream; and at least one heat exchanger, second chiller section, or combination thereof configured to receive and cool the at least the portion of the liquid phase hydrocarbon stream to form the cooled liquid phase hydrocarbon stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising at least one heater, heat exchanger, or combinations thereof configured to receive and heat the cooled second intermediate liquid phase hydrocarbon stream to form a heated second intermediate liquid phase hydrocarbon stream; a stabilizer configured to receive and separate the heated second intermediate liquid phase hydrocarbon stream to form a C₅+ hydrocarbon-rich reformat stream that comprises primarily C₅+ hydrocarbons and a stabilizer gas stream that comprises H₂ and C₄- hydrocarbons; and a stabilizer gas separation zone configured to receive and partially condense and cool at least a portion of the stabilizer gas stream to form a partially condensed stabilizer net gas stream, wherein the stabilizer gas separation zone comprises a separator configured to receive and separate the partially condensed stabilizer net gas stream to form a C₃/C₄ hydrocarbon-rich LPG stream that comprises primarily C₃/C₄ hydrocarbons and a light ends gas stream that comprises H₂ and C₂- hydrocarbons. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first

embodiment in this paragraph, wherein the stabilizer gas separation zone comprises at least one heat exchanger, chiller, cooler, or combination thereof configured to receive and partially condense and cool the at least the portion of the stabilizer gas stream to form the partially condensed stabilizer net gas stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the at least one heat exchanger, chiller, cooler, or combination comprises a stabilizer gas separation zone heat exchanger configured for indirect heat exchange between the cooled second intermediate liquid phase hydrocarbon stream and the at least the portion of the stabilizer gas stream to form a first partially heated, second intermediate liquid phase hydrocarbon stream and the partially condensed stabilizer net gas stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the absorption zone comprises an absorption zone heat exchanger configured for indirect heat exchange between the PSA tail gas hydrocarbon-containing non-permeate residue stream and the first partially heated, second intermediate liquid phase hydrocarbon stream to form a partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream and a second partially heated, second intermediate liquid phase hydrocarbon stream; and a chiller section configured to receive and cool the partially cooled PSA tail gas hydrocarbon-containing non-permeate residue stream to form the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising a stabilizer heat exchanger that is configured for indirect heat exchange between the second partially heated, second intermediate liquid phase hydrocarbon stream and the C5+ hydrocarbon-rich reformat stream to form the heated second intermediate liquid phase hydrocarbon stream, wherein the at least one heater, heat exchanger, or combinations thereof further comprises the stabilizer heat exchanger. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the apparatus is configured to partially heat the cooled second intermediate liquid phase hydrocarbon stream to form a partially heated, second intermediate liquid phase hydrocarbon stream and to combined the partially heated, second intermediate liquid phase hydrocarbon stream with the first intermediate liquid phase hydrocarbon stream to form a combined

liquid phase hydrocarbon stream, wherein the at least one heater, heat exchanger, or combinations thereof is configured to receive and heat the combined liquid phase hydrocarbon stream to form a heated intermediate liquid phase hydrocarbon stream, and wherein the stabilizer is configured to receive and separate the heated intermediate liquid phase hydrocarbon stream to form the C5+ hydrocarbon-rich reformat stream and the stabilizer gas stream.

[0064] A second embodiment of the invention is a method for reforming of hydrocarbons including recovery of products, the method comprising the steps of separating a reforming-zone effluent that comprises H₂, C₄- hydrocarbons, and C₅+ hydrocarbons including aromatics to form a net gas phase stream that comprises H₂ and C₆- hydrocarbons and a liquid phase hydrocarbon stream that comprises C₅+ hydrocarbons including aromatics; separating the net gas phase stream for forming an H₂-rich stream and a first intermediate liquid phase hydrocarbon stream that is enriched with C₃/C₄ hydrocarbons and further comprises C₅+ hydrocarbons; contacting the H₂-rich stream with an adsorbent that selectively separates H₂ from hydrocarbons to form an H₂-ultra rich stream and a pressure swing adsorption (PSA) tail gas stream that comprises H₂, C₂- hydrocarbons, and some C₃+ hydrocarbons; and contacting the PSA tail gas stream with an H₂/hydrocarbon separation membrane to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising the steps of compressing and cooling the PSA tail gas stream to form a further partially cooled, further compressed PSA tail gas stream, and wherein the step of contacting the PSA tail gas stream comprises contacting the further partially cooled, further compressed PSA tail gas stream with the H₂/hydrocarbon separation membrane to form the H₂-ultra rich permeate stream and the PSA tail gas hydrocarbon-containing non-permeate residue stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of compressing and cooling comprises forming the further partially cooled, further compressed PSA tail gas stream having a temperature of from 30 to 150°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the step of

compressing and cooling comprises forming the further partially cooled, further compressed PSA tail gas stream having a pressure of from 1,850 to 3,000 kPa gauge. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising the steps of cooling the PSA tail gas hydrocarbon-containing non-permeate residue stream to form a cooled PSA tail gas hydrocarbon-containing non-permeate residue stream; cooling at least a portion of the liquid phase hydrocarbon stream to form a cooled liquid phase hydrocarbon stream; and contacting the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream with the cooled liquid phase hydrocarbon stream to extract C3/C4 hydrocarbons from the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream to the cooled liquid phase hydrocarbon stream and to form a H₂, C₂-hydrocarbons-containing gas stream and a cooled second intermediate liquid phase hydrocarbon stream that is enriched with C3/C4 hydrocarbons. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein cooling the PSA tail gas hydrocarbon-containing non-permeate residue stream comprises forming the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream having a temperature of from -28 to 4°C.

[0065] A third embodiment of the invention is a method for reforming of hydrocarbons including recovery of products, the method comprising the steps of combining a gas phase stream that comprises H₂ and C₆- hydrocarbons with a liquid phase hydrocarbon stream that comprises C₅+ hydrocarbons including aromatics to extract C3/C4 hydrocarbons from the gas phase stream to the liquid phase hydrocarbon stream to form an H₂-rich stream that comprises primarily H₂ and an intermediate liquid phase hydrocarbon stream that is enriched with C3/C4 hydrocarbons and further comprises C₅+ hydrocarbons; contacting the H₂-rich stream with an adsorbent that selectively separates H₂ from hydrocarbons and that is contained in a pressure swing adsorption (PSA) zone to form an H₂-ultra rich stream and a PSA tail gas stream that comprises H₂, C₂- hydrocarbons, and some C₃+ hydrocarbons; contacting the PSA tail gas stream with an H₂/hydrocarbon separation membrane to separate the PSA tail gas stream and form an H₂-ultra rich permeate stream and a PSA tail gas hydrocarbon-containing non-permeate residue stream; separating the intermediate liquid phase hydrocarbon stream in a stabilizer to form a C₅+ hydrocarbon-rich reformat stream that comprises primarily C₅+ hydrocarbons and a stabilizer gas

stream that comprises H₂ and C₄- hydrocarbons; partially condensing and cooling at least a portion of the stabilizer gas stream to form a partially condensed stabilizer net gas stream; and separating the partially condensed stabilizer net gas stream in a separator to form a C₃/C₄ hydrocarbon-rich LPG stream that comprises primarily C₃/C₄ hydrocarbons and a light ends gas stream that comprises H₂ and C₂- hydrocarbons.

[0066] While at least one exemplary embodiment has been presented in the foregoing detailed description of the disclosure, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the disclosure in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the disclosure. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the disclosure as set forth in the appended claims.

CLAIMS

1. An apparatus (10,210) for reforming of hydrocarbons including recovery of products, the apparatus (10,210) comprising:

5 a separation zone (14) configured to receive and separate a reforming-zone effluent (32) that comprises H_2 , C_4^- hydrocarbons, and C_5^+ hydrocarbons including aromatics to form a net gas phase stream (34) that comprises H_2 and C_6^- hydrocarbons and a liquid phase hydrocarbon stream (36) that comprises C_5^+ hydrocarbons including aromatics;

10 a recovery zone (17,217) configured to receive and separate the net gas phase stream (34) for forming an H_2 -rich stream (92) and a first intermediate liquid phase hydrocarbon stream (58,74) that is enriched with C_3/C_4 hydrocarbons and further comprises C_5^+ hydrocarbons;

15 a pressure swing adsorption (PSA) zone (20) containing an adsorbent for selectively separating H_2 from hydrocarbons, wherein the PSA zone (20) is configured for receiving the H_2 -rich stream (92) and for contacting the H_2 -rich stream (92) with the adsorbent to form an H_2 -ultra rich stream (250) and a PSA tail gas stream (252) that comprises H_2 , C_2^- hydrocarbons, and some C_3^+ hydrocarbons; and

20 a membrane separation zone (16) comprising an H_2 /hydrocarbon separation membrane (201) and configured for receiving the PSA tail gas stream (252) and for contacting the PSA tail gas stream (252) with the H_2 /hydrocarbon separation membrane (201) to form an H_2 -ultra rich permeate stream (202) and a PSA tail gas hydrocarbon-containing non-permeate residue stream (265).

25 2. The apparatus (10,210) of claim 1, wherein the recovery zone (17,217) is configured to receive the H_2 -ultra rich permeate stream (202) with the net gas phase stream (34) for forming the H_2 -rich stream (92) and the first intermediate liquid phase hydrocarbon stream (58,74).

30 3. The apparatus (10,210) of claim 1, further comprising an absorption zone (21) configured to receive and cool the PSA tail gas hydrocarbon-containing non-permeate residue stream (265) and at least a portion of the liquid phase hydrocarbon stream (36) to form a cooled PSA tail gas hydrocarbon-containing non-permeate residue stream (272) and a cooled liquid phase hydrocarbon stream (278), respectively, wherein the absorption

zone (21) comprises an absorber (25) that is configured for contacting the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream (272) with the cooled liquid phase hydrocarbon stream (278) to extract C₃/C₄ hydrocarbons from the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream (272) to the cooled liquid phase hydrocarbon stream (278) to form a H₂, C₂⁻ hydrocarbons-containing gas stream (204) and a cooled second intermediate liquid phase hydrocarbon stream (280) that is enriched with C₃/C₄ hydrocarbons.

4. The apparatus (10,210) of claim 3, further comprising at least one compressor and at least one cooler, heat exchanger, or combinations thereof cooperatively configured to receive the PSA tail gas stream (252) and to compress and partially cool the PSA tail gas stream (252) to form a further partially cooled, further compressed PSA tail gas stream (262), and wherein the membrane separation zone (16) is configured to receive the further partially cooled, further compressed PSA tail gas stream (262) for contact with the H₂/hydrocarbon separation membrane (201) to form the H₂-ultra rich permeate stream (202) and the PSA tail gas hydrocarbon-containing non-permeate residue stream (265).

5. The apparatus (10,210) of claim 4, further comprising a dryer (261) that is cooperatively arranged with the at least one compressor and the at least one cooler, heat exchanger, or combinations thereof so as to remove water from the PSA tail gas stream (252) before the further partially cooled, further compressed PSA tail gas stream (262) is introduced to the membrane separation zone (16).

6. The apparatus (10,210) of claim 4, wherein the at least one compressor and the at least one cooler, heat exchanger, or combinations thereof are cooperatively configured to receive the PSA tail gas stream (252) and to compress and partially cool the PSA tail gas stream (252) to form a partially cooled, further compressed PSA tail gas stream, and wherein the at least one cooler, heat exchanger, or combinations thereof comprises a PSA tail gas heat exchanger (260) that is configured for indirect heat exchange between the partially cooled, further compressed PSA tail gas stream and the H₂, C₂⁻ hydrocarbons-containing gas stream (204) to form the further partially cooled, further compressed PSA

tail gas stream (262) and a partially heated H_2 , C_2^- hydrocarbons-containing gas stream (204).

7. The apparatus (10,210) of claim 3, wherein the absorption zone (21) comprises:

5 at least one heat exchanger, first chiller section, or combinations thereof configured to receive and cool the PSA tail gas hydrocarbon-containing non-permeate residue stream (265) to form the cooled PSA tail gas hydrocarbon-containing non-permeate residue stream (272); and

10 at least one second chiller section configured to receive and cool the at least the portion of the liquid phase hydrocarbon stream (36) to form the cooled liquid phase hydrocarbon stream (278).

8. The apparatus (10,210) of claim 3, further comprising:

15 at least one heater, heat exchanger, or combinations thereof configured to receive and heat the cooled second intermediate liquid phase hydrocarbon stream (280) to form a heated second intermediate liquid phase hydrocarbon stream (104);

20 a stabilizer (22) configured to receive and separate the heated second intermediate liquid phase hydrocarbon stream (104) to form a C_5^+ hydrocarbon-rich reformat stream (102) that comprises primarily C_5^+ hydrocarbons and a stabilizer gas stream (106) that comprises H_2 and C_4^- hydrocarbons; and

a stabilizer gas separation zone (23) configured to receive and partially condense and cool at least a portion of the stabilizer gas stream (106) to form a partially condensed stabilizer net gas stream (291), wherein the stabilizer gas separation zone (23) comprises:
25 a separator (124) configured to receive and separate the partially condensed stabilizer net gas stream (291) to form a C_3/C_4 hydrocarbon-rich LPG stream (126) that comprises primarily C_3/C_4 hydrocarbons and a light ends gas stream (128) that comprises H_2 and C_2^- hydrocarbons.

9. The apparatus (10,210) of claim 8, wherein the stabilizer gas separation zone (23) comprises at least one heat exchanger, chiller, cooler, or combination thereof configured to
30 receive and partially condense and cool the at least the portion of the stabilizer gas stream (106) to form the partially condensed stabilizer net gas stream (291).

10. The apparatus (10,210) of claim 9, wherein the at least one heat exchanger, chiller, cooler, or combination comprises a stabilizer gas separation zone heat exchanger (89) configured for indirect heat exchange between the cooled second intermediate liquid phase hydrocarbon stream (280) and the at least the portion of the stabilizer gas stream (106) to form a first partially heated, second intermediate liquid phase hydrocarbon stream (270) and the partially condensed stabilizer net gas stream (291).
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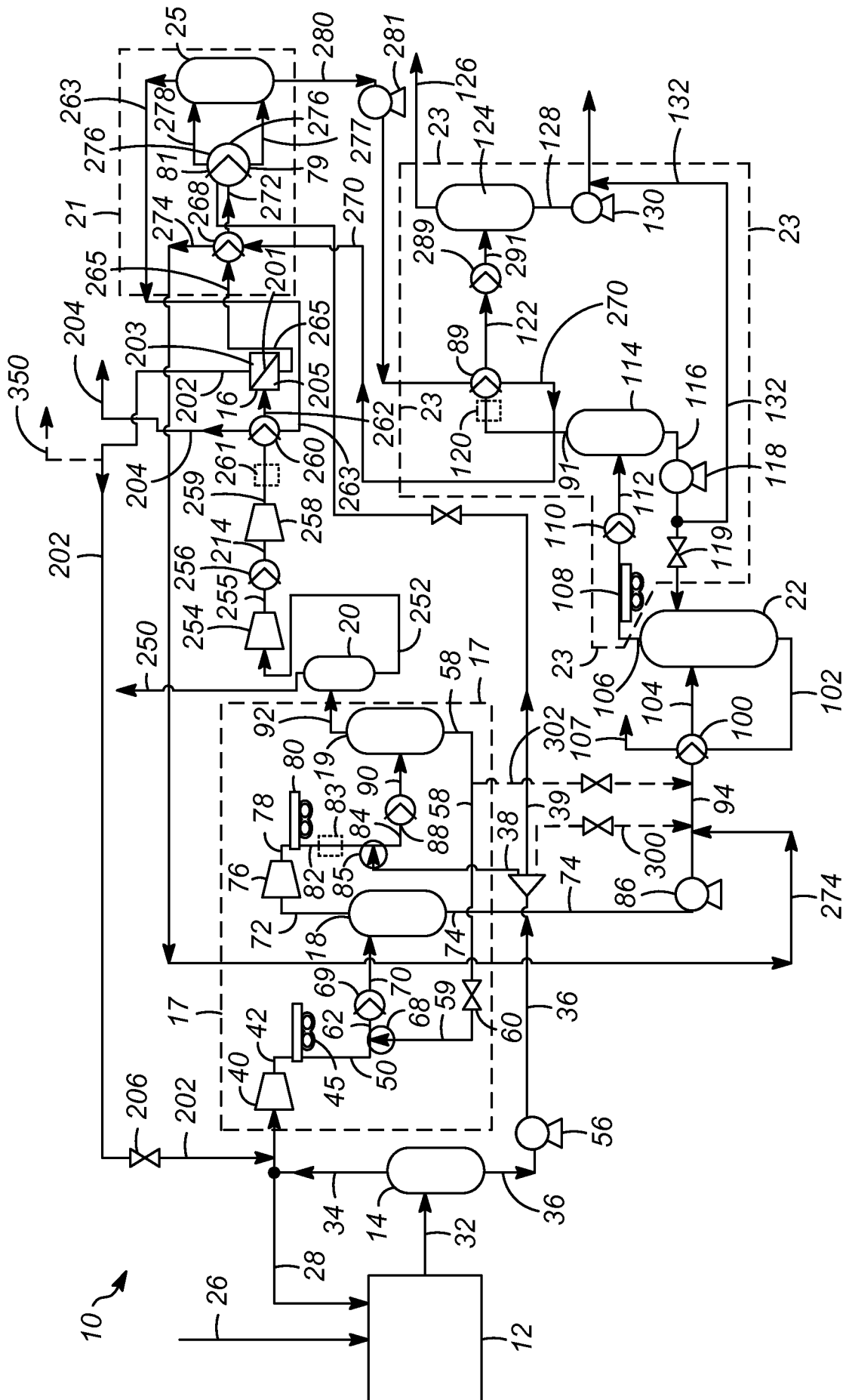


FIG. 1

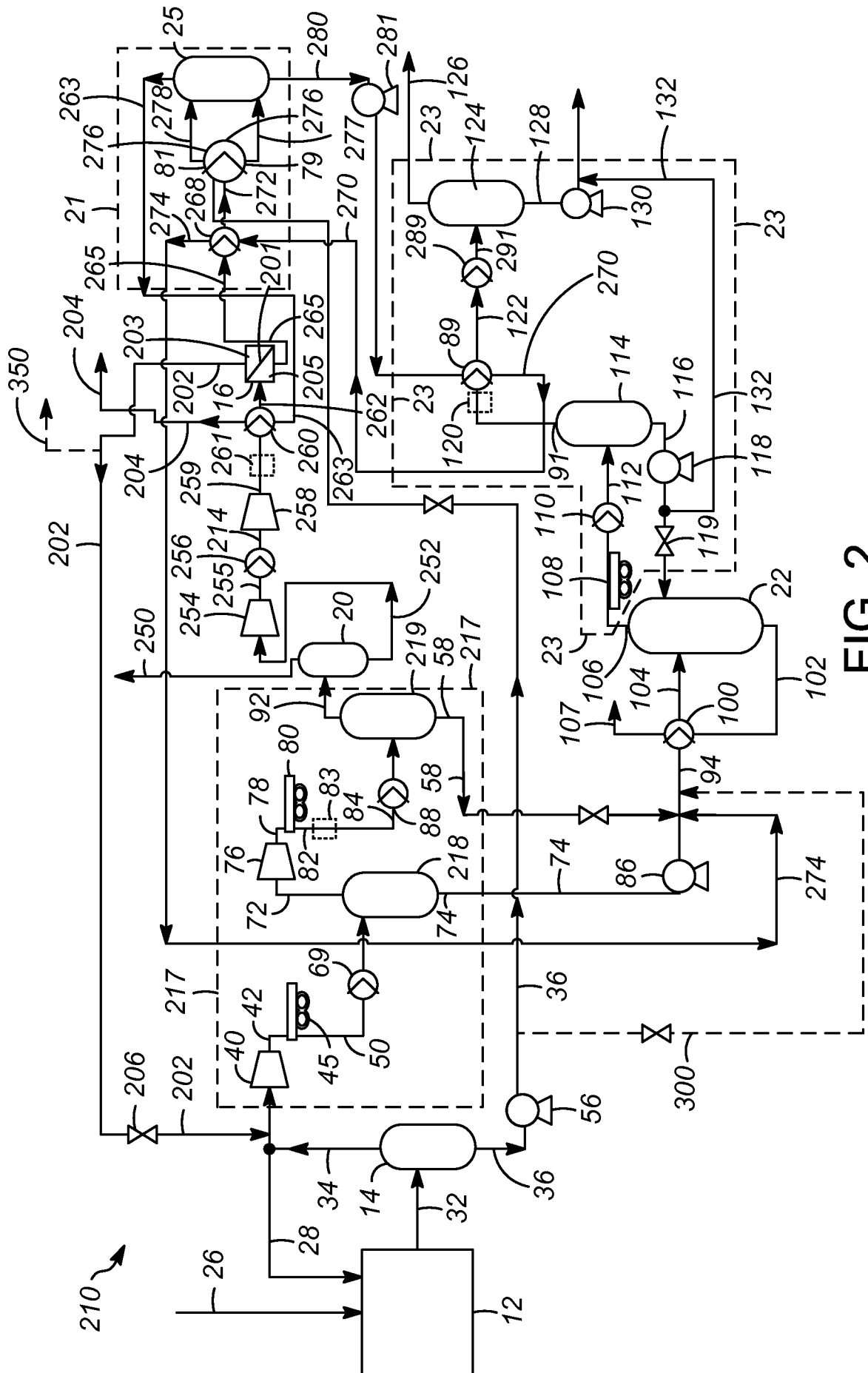


FIG. 2