

AROMATIZATION OF NON-AROMATIC HYDROCARBON**CROSS REFERENCE TO RELATED APPLICATIONS**

5 [0001] This invention claims priority to and the benefit of U.S. Patent Application Serial Nos. 62/232,609 filed September 25, 2015 and 62/253,268 filed November 10, 2015 entitled AROMATIZATION OF NON-AROMATIC HYDROCARBONS; and European Patent Application Nos. 15195311.4 filed November 19, 2015, all of which are herein incorporated by reference in their entireties.

10 [0002] The following related cases are also incorporated by reference in their entireties: U.S. Patent Application Serial No. 62/234,262, filed September 29, 2015; European Patent Application No. 15195314.8, filed November 19, 2015; U.S. Patent Application Serial No. 62/234,240, filed September 29, 2015; European Patent Application No. 15197698.2, filed December 3, 2015; U.S. Patent Application Serial No. 62/247,795, filed October 29, 2015; European Patent Application No. 15197700.6, filed December 03, 2015; U.S. Patent Application Serial No. 62/248,374, filed October 30, 2015; European Patent Application No. 15197702.2, filed December 3, 2015; U.S. Patent Application Serial No. 62/253,268, filed November 10, 2015; U.S. Patent Application Serial No. 62/326,918, filed April 25, 2016; European Patent Application No. 16175163.1, filed June 20, 2016; U.S. Patent Application Serial No. 62/299,730, filed February 25, 2016; European Patent Application No. 16167395.9, filed April 28, 2016; U.S. Patent Application Serial No. 62/313,288, filed March 25, 2016; European Patent Application No. 16173587.3, filed June 8, 2016; U.S. Patent Application Serial No. 62/313,306, filed March 25, 2016; European Patent Application No. 16173980.0, filed June 10, 2016; U.S. Patent Application Serial No. 62/298,655, filed February 23, 2016; and European Patent Application No. 16167672.1, filed April 29, 2016.

25 FIELD

[0003] The systems and methods described herein relate to aromatization of non-aromatic hydrocarbon, to equipment and materials useful in such aromatization, and to the use of such aromatization for, e.g., natural gas upgrading.

BACKGROUND

30 [0004] Improved production methods have led to an increase in the availability of hydrocarbon gasses of geological origin, e.g., natural gas. Natural gas generally comprises a

mixture of one or more hydrocarbon compounds having a number of carbon atoms in the range of from C₁ to C₉, and can further comprise non-hydrocarbon compounds such as CO₂ and/or H₂S. Natural gas is used for a wide variety of purposes, e.g., electric power generation, transportation fuel, residential and commercial heating and cooking, and as a feed stock for producing commodity chemicals such as ethylene.

[0005] Frequently, natural gas is produced from a geological formation that is located some distance away from the place at which it is consumed. This has stimulated the construction of natural gas pipelines, which transport compressed natural gas from producers to consumers. Some natural gas consumers, e.g., operators of electric power generators, are sensitive the caloric content of the natural gas obtained from the pipeline. When the natural gas has too little caloric content, the electric power generators operate inefficiently. Too large a caloric content can lead to equipment damage, e.g., as a result of overheating the generator's combustion and expansion stages.

[0006] To avoid these difficulties, pipeline operators have established specifications for natural gas entering the operator's pipeline. Heating value, which is a measure of the caloric content of a natural gas, is one typical pipeline specification. Another is Wobbe Index, which is closely related to natural gas combustion energy. Two different natural gasses obtained from different sources and having different compositions, but having substantially the same Wobbe Index, will have substantially the same combustion heat output when combusted under substantially the same conditions. As an example, a pipeline operator might require that natural gas entering its pipeline have a heating value of from 36.07 MJ/sm³ to 41.40 MJ/sm³) and a Wobbe Index of from 49.01 MJ/sm³ to 52.22 MJ/sm³).

[0007] The heating value and Wobbe Index of a natural gas are strongly influenced by the type and relative amounts of the gas's hydrocarbon compounds. Typically, hydrocarbon compounds having a greater number of carbon atoms provide an increased heat of combustion. Consequently, when a natural gas does not meet the minimum heating value and Wobbe Index specifications, propane enrichment can be used to produce a pipeline-able gas. More typically, the natural gas exceeds the heating value and Wobbe Index specifications. In these cases, a natural gas producer might extract a portion of the gas's relatively-high heating content hydrocarbon compounds, e.g., excess ethane and/or excess propane beyond that needed to achieve the minimum specified heating value and Wobbe Index.

[0008] Fractionation and dew point control are conventional methods for producing a pipeline-able natural gas from a natural gas source that does not meet the pipeline's heating

value and Wobbe Index specifications. For example, a natural gas of excessive Wobbe Index and/or heating value can be fractionated to produce a bottoms fraction comprising primarily C₅₊ hydrocarbon, a side stream comprising primarily C₃ and C₄ hydrocarbon, and an overhead stream comprising primarily methane and ethane. The bottoms fraction is typically conducted away, e.g., for blending with other liquid hydrocarbon. In locations having the facilities to do so, the side stream can be compressed and transported as LPG. In remote locations, the side stream is typically re-injected into the reservoir. The fractionation is configured to produce a methane/ethane mixture that meets pipeline specifications. Since the composition of natural gas and the relevant pipeline specifications vary from location to location, fractionation conditions cannot be readily standardized. In part as a result of this difficulty, fractionation is typically utilized when the natural gas is in the form of a raw natural gas produced from a natural gas well ("gas well gas"), particularly those having a lesser C₃₊ hydrocarbon content.

[0009] Dew point control is typically used when the natural gas has a greater C₃₊ hydrocarbon content, e.g., when the natural gas is associated gas. Associated gas is a form of natural gas that is typically found with petroleum deposits, e.g., dissolved in the oil or as a free "gas cap" above the oil in a reservoir. To carry out dew point control, a mixture of gaseous and liquid hydrocarbon produced from a reservoir is conducted to a vapor-liquid separation stage. A bottoms product comprising crude oil is conducted away. An overhead stream comprising associated gas is also conducted away, at least a portion of which is conducted to the dew point control stage. Dew point control is carried out by cooling the associated gas to a sufficiently low temperature at a sufficiently elevated pressure to condense a sufficient portion thereof such that the remaining vapor-phase portion meets pipeline specifications at that location. The liquid-phase is disengaged from the vapor phase in, e.g., a separator drum. A pipeline-able natural gas comprising primarily methane and ethane is conducted away from the separator drum as an overhead stream. A bottoms stream comprising primarily C₂₊ hydrocarbon is also conducted away. It is conventional to convert at least a portion of the bottoms stream to aromatic hydrocarbon, which greatly lessens difficulties associated with transporting the bottoms stream away from remote locations. See, e.g., P.C.T. Patent Application Publication No. WO 2015/084518A1, which is incorporated by reference herein in its entirety.

[0010] One aromatization process, disclosed in U.S. Patent No. 4,855,522, involves converting C₂, C₃, and C₄ hydrocarbon with increased selectivity for aromatic hydrocarbon. The process utilizes a dehydrocyclization catalyst including (a) an aluminosilicate having a

silica to alumina molar ratio of at least 5 and (b) a compound of (i) Ga and (ii) at least one rare earth metal. The reference discloses carrying out the aromatization conversion at a space velocity (LHSV) in the range of from 0.5 to 8 hr⁻¹, a temperature $\geq$ 450 °C (e.g., 475 °C to 650 °C), a pressure of from 1 bar to 20 bar, and a feed contact time of 1 to 50 seconds. One
5 difficulty observed with this process is that the accumulation of catalyst coke gradually decreases aromatic hydrocarbon yield. One way to overcome this difficulty includes operating the reaction cyclically, e.g., by carrying out the reaction in at least two reactors. The first reactor carries out aromatization (reaction mode) while the second reactor undergoes decoking (regeneration mode), and *vice versa*. Decreasing the amount of time (the “cycle time”) that a
10 fixed bed reactor is operated in reaction mode before switching to regeneration mode is used to lessen the amount of coke accumulation. However, decreasing cycle time decreases the yield of aromatic hydrocarbon produced by the process, particularly when a significant amount of coke has accumulated. In those cases, it can be necessary to carry out regenerating mode for a relatively long time interval compared to that of aromatization mode. Another way to
15 overcome this difficulty involves utilizing fluidized catalyst beds in the reaction stages. This, however, typically requires specialized catalysts and process conditions, and is difficult to implement in practice, particularly in remote locations.

[0011] Still other difficulties encountered when operating conventional process for natural gas aromatization arise from the compositional variation observed for natural gas produced in
20 different locations. Some natural gas is relatively rich in ethane; other natural gas contains much less. It is observed when operating conventional aromatization of C₂ – C₄ hydrocarbon that conditions needed for C₂ aromatization typically lead to excessive conversion to coke of the C₃ and C₄ hydrocarbon. Further, conditions optimized for the aromatization of C₃ and C₄ hydrocarbon typically exhibit less aromatics yield from the natural gas’s C₂ hydrocarbon. This
25 situation is worsened by the wide variation in ethane content of natural gas produced from different reservoirs.

[0012] One way to overcome this is to tailor the aromatization process so that it is compatible with a particular reservoir. For example, U.S. Patent No. 8,835,706 discloses aromatization of an ethane-propane feed in two reactors operated in a complex series/parallel
30 arrangement. The feed to the process, which is obtained from natural gas by cryogenically separating methane, is reacted in a first stage operated under conditions which maximize the conversion of propane to aromatics. Ethane is reacted in the second stage to produce additional aromatics. The second stage is operated under conditions which maximize the conversion of

ethane to aromatic hydrocarbon. The process can be tailored to a particular natural gas source by, e.g., appropriately sizing the first, reactor, second reactor, and associated interconnection and separations stages. Doing so, however, limits the usefulness of the process to natural gas within a relatively narrow compositional range.

- 5 **[0013]** There is therefore a need for improved processes for aromatizing $C_2 - C_9$ non-aromatic hydrocarbon, such as those extracted from natural gas. More particularly, there is a need for aromatization processes that are capable of operating at relatively long cycle time, and which avoid the complexities of conventional process. Even more desired are aromatization processes that do not require tailoring reactors and associated equipment to the composition of
- 10 a particular source of $C_2 - C_9$ hydrocarbon, and especially processes that can be carried out using standardized modules that are readily transported to remote locations.

SUMMARY

- [0014]** The invention generally relates to upgrading gaseous hydrocarbon of different composition, as may be produced from various sources at various geographic locations. The
- 15 sources each comprise methane, C_2 hydrocarbon and C_{3+} non-aromatic hydrocarbon but contain significantly different relative amounts of these components. Controlling the volumetric flow rate of such a gaseous hydrocarbon from the source in an inverse relationship with the hydrocarbon source's C_{2+} hydrocarbon concentration upstream of a separation stage is found to provide a separated C_{2+} hydrocarbon stream having desirable features. The
- 20 separated C_{2+} hydrocarbon stream features both a substantially-constant volumetric flow rate and a substantially constant C_{2+} hydrocarbon concentration. Advantageously, it has been discovered that these features are achieved for a wide variety of gaseous hydrocarbon, as may be produced at a wide variety of geographic locations by a wide variety of processes.

- [0015]** This discovery has led to the development of a system and process which includes
- 25 at least two main functionalities: an aromatization functionality and a product recovery functionality. The aromatization functionality is configured to receive a gaseous aromatization feed having (i) a preselected volumetric flow rate and (ii) a preselected concentration of C_{2+} non-aromatic hydrocarbon. The aromatization functionality produces a reaction effluent comprising aromatic hydrocarbon produced by dehydrocyclization of at least a portion of the
- 30 aromatization feed's C_{2+} non-aromatic hydrocarbon. The product recovery functionality separates at least aromatic hydrocarbon from the reaction effluent. The process is advantageous in that it can be operated at relatively long cycle times without the complexities of conventional process. Since the aromatization functionality is configured for aromatizing a

preselected volumetric flow rate of an aromatization feed having a predetermined concentration of C₂₊ hydrocarbon, the process can be carried out in modules configured for the specified functionalities, e.g., using individual feed pre-treatment, aromatization, and product recovery modules configured for performing those functions. The modules, which can be of a
5 preselected size and capacity, can be readily transported to a wide variety of remote locations, e.g., for natural gas processing.

DESCRIPTION OF THE DRAWINGS

- [0016] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:
- 10 [0017] Fig. 1 is a block diagram of a modular system for producing a product comprising aromatic hydrocarbon.
- [0018] Fig. 2 is a simplified process flow diagram illustrating certain aspects of the invention.
- [0019] Fig. 3 is a process flow diagram featuring an aromatizer having two
15 dehydrocyclization stages.

DETAILED DESCRIPTION

- [0020] Although certain aspects of the invention are described in greater detail, the invention is not limited thereto, and this description is not meant to foreclose other aspects within the within the true spirit and scope of the appended claims.
- 20 [0021] Certain aspects of the systems and techniques described herein relate to hydrocarbon conversion utilizing an aromatizer, a recoverer, and an optional pretreater. The hydrocarbon conversion utilizes a gaseous feed comprising C₂ hydrocarbon and C₃₊ non-aromatic hydrocarbon. The gaseous feed is treated in the feed pretreater, to provide an aromatization feed for aromatization, the gaseous aromatization feed having (i) a preselected
25 volumetric flow rate and (ii) a preselected concentration of C₂₊ non-aromatic hydrocarbon. The feed pretreatment can be carried out in stages, e.g., by transferring heat away from the gaseous feed in a heat transfer stage in order to condense a portion of the gaseous feed. A separation stage can be used for separating condensate from the remainder of the gaseous feed which comprises gaseous hydrocarbon. The aromatization feed is produced by vaporizing at least a
30 portion of the condensate. Condensate vaporization can be carried out at any convenient location, typically upstream of the dehydrocyclization reaction. The form of heat transfer used is not critical, and can be direct, indirect, or a combination thereof. The form of separation is

not critical, and can include one or more fractionators, one or more separator drums, one or more membranes, or a combination thereof. Conventional heat transfer and separation technology can be used, but the invention is not limited thereto. For gaseous feeds available from a wide variety of sources at a wide variety of geographic locations, the amount of gaseous feed condensation can be regulated so that the pretreatment produces a preselected volumetric flow rate of aromatization feed, with the aromatization feed having a preselected concentration of C₂₊ non-aromatic hydrocarbon. Advantageously, the preselected values are substantially constant, e.g., no significant variation is needed to practice the invention using gaseous feeds available at different geographic locations.

- 10 [0022] This can be accomplished, e.g., by one or more of (i) decreasing the volumetric flow rate of gaseous feed to the pretreatment at geographic locations where the gaseous feed has a greater concentration of C₂₊ non-aromatic hydrocarbon, (ii) increasing the volumetric flow rate of gaseous feed at geographic locations where the gaseous feed has a lesser concentration of C₂₊ non-aromatic hydrocarbon, (iii) decreasing the amount of heat withdrawn from the gaseous feed at geographic locations where the gaseous feed has a greater concentration of C₂₊ non-aromatic hydrocarbon, (iv) increasing the amount of heat withdrawn from the gaseous feed at geographic locations where the gaseous feed has a lesser concentration of C₂₊ non-aromatic hydrocarbon, (v) increasing the gaseous feed's pressure at geographic locations where the gaseous feed has a lesser concentration of C₂₊ non-aromatic hydrocarbon, and (vi) decreasing the gaseous feed's pressure at geographic locations where the gaseous feed has a greater concentration of C₂₊ non-aromatic hydrocarbon.

- 25 [0023] Since the preselected volumetric flow rate and the preselected concentration of C₂₊ non-aromatic hydrocarbon are substantially independent of the gaseous feed utilized, the capacities (e.g., hydraulic capacity) of the pretreatment, reaction, and recovery functionalities can be preselected, in the sense that these capacities can be substantially the same for any geographic location where a suitable gaseous feed may be available. Advantageously, this permits the standardization of the pretreatment, reaction, recovery, and auxiliary functionalities. For example, one or more of these functionalities can be modularized, e.g., a functionality can be carried out in one or more modules of standardized size, shape, and/or capacity. Conventional separators, aromatizers, and recoverers are customized for conversion of a gaseous feed in a particular geographic location. Unlike the conventional case, the pretreater, aromatizer, and recoverer of the invention are standardized. Where a greater conversion capacity is needed in a particular geographic location, fewer standardized

pretreaters, aromatizers, and recoverers can be used (e.g., fewer standard modules for one or more of these functionalities). In locations where a greater conversion capacity is needed, a greater number of standardized aromatizers, pretreaters, aromatizers, and recoverers can be used (e.g., more standardized modules for one or more of these functionalities). In other words, one advantage of the invention is that it compensates for variations in needed conversion capacity by increasing or decreasing capacity in discreet, standardized amounts, instead of requiring customization by continuous capacity variation as in the prior art.

[0024] The aromatization feed is reacted in the presence of a catalytically effective amount of at least one dehydrocyclization catalyst under dehydrocyclization conditions. The reaction converts at least a portion of the aromatization feed's non-aromatic hydrocarbon aromatic hydrocarbon and optionally other cyclic hydrocarbon. The number of reactors utilized for carrying out the reaction is not critical, nor is the number of catalyst beds in each reactor. When the dehydrocyclization reaction is carried out in a plurality of reactors, a portion of the aromatic hydrocarbon produced in a first reactor may be removed before the remainder of the first reactor's effluent is reacted in one or more additional reactors. In other aspects, the first reactor's reaction effluent may be reacted in one or more additional reactors with little or no separation of aromatic hydrocarbon from the first reaction effluent. The presence of the first product's aromatic hydrocarbon and methane in the second stage is less detrimental to additional aromatic hydrocarbon production than may be expected from the teachings of the prior art.

[0025] The pretreatment, reaction, recovery, and auxiliary functionalities will now be described in more detail. To avoid doubt about the meaning of certain terms used in this description and appended claims, the following definitions are provided.

Definitions

[0026] Two or more items are, "proximate" to one another when they are spatially close, without regard to whether the spatial relationship places one item underneath, over, or beside another item. Items of definite size and/or shape (e.g., physical components) can be proximate to one another and/or proximate to items that might be of indefinite size and/or shape (e.g., certain chemical reactions).

[0027] As used herein, "substantially" or other words of degree are relative modifiers intended to indicate permissible variation from the characteristic so modified. It is not intended to be limited to the absolute value or characteristic which it modifies, but rather possessing

more of the physical or functional characteristic than its opposite, and preferably, approaching or approximating such a physical or functional characteristic. Unit conversions to Normal Meters³ per Day (“NM³D”) of a gaseous composition, and to m³ per day (“M³PD”) of a liquid composition, use conversion factors from the Petroleum Engineering Handbook, Vol. VII, Indexes and Standards, 169, Society of Petroleum Engineers, 2007.

[0028] The term “C_n” hydrocarbon means hydrocarbon having n carbon atom(s) per molecule, wherein n is a positive integer. The term “C_{n+}” hydrocarbon means hydrocarbon having at least n carbon atom(s) per molecule. The term “C_{n-}” hydrocarbon means hydrocarbon having no more than n carbon atom(s) per molecule. The term “hydrocarbon” means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon, (ii) unsaturated hydrocarbon, and (iii) mixtures of hydrocarbons, and including mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n. A “Gaseous” composition is one that is primarily in the vapor phase.

[0029] The terms “alkane” and “paraffinic hydrocarbon” mean substantially-saturated compounds containing hydrogen and carbon only, e.g., those containing ≤ 1% (molar basis) of unsaturated carbon atoms. As an example, the term alkane encompasses C₂ to C₂₀ linear, iso, and cyclo-alkanes. Aliphatic hydrocarbon means hydrocarbon that is substantially free of hydrocarbon compounds having carbon atoms arranged in one or more rings.

[0030] The term “unsaturate” and “unsaturated hydrocarbon” refer to one or more C₂₊ hydrocarbon compounds which contain at least one carbon atom directly bound to another carbon atom by a double or triple bond. The term “olefin” refers to one or more unsaturated hydrocarbon compound containing at least one carbon atom directly bound to another carbon atom by a double bond. In other words, an olefin is a compound which contains at least one pair of carbon atoms, where the first and second carbon atoms of the pair are directly linked by a double bond. The term “aromatics” and aromatic hydrocarbon mean hydrocarbon compounds containing at least one aromatic core.

[0031] The term “Periodic Table” means the Periodic Chart of the Elements, as it appears on the inside cover of The Merck Index, Twelfth Edition, Merck & Co., Inc., 1996.

[0032] The term “reaction zone” or “reactor zone” mean a location within a reactor, e.g., a specific volume within a reactor, for carrying out a specified reaction. A reactor or reaction stage can encompass one or more reaction zones. More than one reaction can be carried out in

a reactor, reactor stage, or reaction zone. For example, a reaction stage can include a first zone for carrying out first and second reactions and a second zone for carrying out a third reaction, where the first reaction (e.g., dehydrocyclization) can be the same as or different from the second reaction, and the third reaction (e.g., selective oxidation) can be the same as or different from the second reaction.

5 [0033] “Dehydrocyclization” means removing hydrogen from and cyclizing a non-cyclic hydrocarbon to produce, e.g., one or more of cyclo-paraffin, cyclo-olefin, and aromatic hydrocarbon. The reaction can be carried out in one or more of (i) one step, which includes both dehydrogenation and cyclization; (ii) two steps, e.g., dehydrogenation followed by
10 cyclization of the dehydrogenated intermediate; and (iii) three or more steps, e.g., normal paraffin dehydrogenation, cyclization of the olefinic intermediate, and additional dehydrogenation (aromatization) of the cyclo-olefin intermediate. The dehydrocyclization (including any dehydrogenation carried out in connection with dehydrocyclization) is “non-oxidative” meaning that the reaction is carried out with little if any oxidative coupling of feed
15 hydrocarbon, intermediate hydrocarbon (if any), or dehydrocyclization product.

[0034] The term “selectivity” refers to the production (on a weight basis) of a specified compound in a catalytic reaction. As an example, the phrase “a light hydrocarbon conversion reaction has a 100% selectivity for aromatic hydrocarbon” means that 100% of the light hydrocarbon (weight basis) that is converted in the reaction is converted to aromatic
20 hydrocarbon. When used in connection with a specified reactant, the term “conversion” means the amount of the reactant (weight basis) consumed in the reaction. For example, when the specified reactant is C₄ paraffinic hydrocarbon, 100% conversion means 100% of the C₄ paraffinic hydrocarbon is consumed in the reaction. The yield, on a weight basis, is the product of the conversion and the selectivity.

25 [0035] The term “modularization” means to arrange process equipment and associated piping, valving, instrumentation, controls and support systems into compact and transportable units. Such a unit or plurality thereof can be supported on one or more moveable skids. Modularization desirably provides operational flexibility. Processing capacity is readily increased, e.g., by adding additional modules.

30 [0036] Certain aspects of the invention, which include processing hydrocarbon of geological origin, will now be described in more detail with reference to Fig. 1. The invention is not limited to these aspects, and this description is not meant to foreclose other aspects within the broader scope of the invention, such as those where the gaseous feed is obtained from

chemical and/or refining processes such as one or more of coking, catalytic cracking, catalytic reforming, and/or steam cracking.

[0037] Fig. 1 schematically illustrates a system **100** for converting to aromatic hydrocarbon non-aromatic hydrocarbon contained in a gaseous feed. A hydrocarbon source **102** is provided, e.g., a mixture of gaseous and liquid hydrocarbon such as a mixture of natural gas and crude oil produced from a reservoir. Hydrocarbon from the hydrocarbon source is conducted to separator **104** for separation of at least a raw natural gas and a liquid, the liquid comprising, e.g., crude oil. The raw natural gas is conducted away via conduit **116**. The liquid, which can contain entrained solids, liquids, and gases, e.g., entrained water, organic compounds, metals, etc., is conducted away via conduit **106** to stabilizer **108**. Liquid stabilization includes the removal from the liquid of various contaminants, such as water, light hydrocarbons, and gas contaminants. Typically, sufficient of these species are boiled-off or otherwise removed to produce a stabilized liquid stream **110** which meets applicable crude oil specifications, e.g., specifications relating to vapor pressure, water content, and sediment content. In addition to the stabilized liquid stream, a vapor stream is also separated from the liquid entering stabilizer **108**. The separated vapor, typically comprising C₉- non-aromatic hydrocarbon, is conducted away from the stabilizer via conduit **112**. The raw natural gas of conduit **116** is combined with the separated vapor of conduit **112** to form the gaseous feed, which is conducted via conduit **118** to pretreater **114**.

[0038] At least two streams are conducted away from pretreater **114**. The first stream is the aromatization feed, which is produced at a preselected volumetric flow rate, and which has a preselected concentration of C₂+ non-aromatic hydrocarbon. The second stream, which comprises mainly methane and ethane, has been found to meet heating value and Wobbe Index specifications of a variety of natural gas pipelines. The first stream is conducted away via conduit **120** (e.g., as condensed liquid and/or vapor) to aromatizer **124**. The second stream is conducted away via conduit **115**, e.g., for one or more of storage; transportation, e.g., via pipeline; further processing, e.g., cooling/compression to produce a compressed gas and/or LNG; re-injection into hydrocarbon source **102**; etc. In addition to the first and second streams, a primarily liquid third stream comprising hydrocarbon is optionally produced and conducted away from the pretreater via conduit **122**. The third stream can be generated in aspects in which the pretreater includes at least one fractionator (e.g., one or more distillation columns), where the third stream can be, e.g., a fractionator bottoms stream.

[0039] The aromatization feed is conducted via conduit **120** to aromatizer **124**, for

conversion to aromatic hydrocarbon of at least a portion of the feed's C₂+ non-aromatic hydrocarbon. A reaction effluent is conducted away via conduit **126**. The reaction effluent comprises (i) non-aromatic hydrocarbon and (ii) aromatic hydrocarbon and molecular hydrogen, at least a portion of the aromatic hydrocarbon and the molecular hydrogen (and
5 optionally a portion of the non-aromatic hydrocarbon) being formed during the dehydrocyclization.

[0040] The reaction effluent is conducted via conduit **126** to recoverer **128**, for recovering at least a first product and a tail gas from the reaction effluent. The first product comprises at least a portion of the reaction effluent's aromatic hydrocarbon. The tail gas comprises (i) at
10 least a portion of the reaction effluent's molecular hydrogen and (ii) at least a portion of the reaction effluent's non-aromatic hydrocarbon. The tail gas, which typically comprises primarily molecular hydrogen, methane, and ethane, is conducted away via conduit **130**, e.g., for one or more of storage; transportation, such as via pipeline; further processing, e.g., cooling/compression to produce a compressed gas and/or LNG; re-injection into hydrocarbon
15 source **102**; etc. Since the tail gas has been found to meet heating value and Wobbe Index specifications of a variety of natural gas pipelines, in certain aspects (not shown) at least a portion of the tail gas is combined with at least a portion of the pretreater's second stream, e.g., for pipeline transportation of the combined stream. In the aspects illustrated schematically in Fig. 1, the tail gas is conducted via conduit **130** to hydrogen separator **142**.

20 **[0041]** As shown in Fig. 1, the first product, comprising recovered aromatic hydrocarbon, is conducted away via conduit **138**. Valve means, V₁ and V₂, can be used for (i) diverting all or a portion of the first product away from the process for storage, transportation, or further processing and/or (ii) combining all or a portion of the first product with liquid stream **110**.

[0042] Tail gas, in addition to molecular hydrogen, methane, and ethane, can further
25 comprise sulfur compounds such as mercaptan and/or hydrogen sulfide. Typically, this is the case when the aromatization feed includes organosulfur compounds, H₂S, or both. If desired, the tail gas can be treated (not shown in Fig. 1) to remove at least a portion of any sulfur compounds as may be present. Sulfur removal can be carried out before the tail gas is introduced into conduit **130**, and/or thereafter. Conventional sulfur removal technology can be
30 used, but the invention is not limited thereto. Although sulfur removal is optional, it is typically carried out when the tail gas comprises ≥ 4 ppm H₂S, e.g., ≥ 1000 ppm, such as ≥ 1 %, particularly in aspects where at least a portion of the tail gas is subjected to additional dehydrocyclization.

[0043] All or a portion of the tail gas can be utilized for on-site power generation, e.g., by combusting tail gas in one or more gas turbines, the gas turbine being used to power one or more electric generators of power generator **140**. The electricity can be used in the process, e.g., for heating aromatizer **124**, e.g., to provide heat for the (typically endothermic) dehydrocyclization reaction. Alternatively, or in addition, the electricity generated can be introduced into one or more power grids. Alternatively or in addition to the gas turbine, one or more combustion engines can be used for combusting tail gas, e.g., to power the electric generator.

[0044] In particular aspects illustrated in Fig. 1, molecular hydrogen is separated from the tail gas upstream of power generator **140**, with at least a portion of the separated molecular hydrogen being conducted via conduit **144** to power generator **140**. Typically, the separated molecular hydrogen is conveyed to power generator **140** together with other tail gas components such as methane and/or ethane. Such a combined stream is referred to as a hydrogen-rich stream because it has a greater molecular hydrogen content than does the tail gas from which it was separated. After molecular hydrogen separation, the remainder of the tail gas constitutes a hydrogen-lean stream. Conveying the hydrogen-rich stream from hydrogen separator **142** to power generator **140** can be desirable, e.g., when the tail gas has too low a BTU content for efficient power generation, or if a lesser amount of generated power is desired. Conventional hydrogen separation technology can be utilized in hydrogen separator **142**, but the invention is not limited thereto. Typically, the hydrogen-rich stream comprises ≥ 50 wt. % of the tail gas's molecular hydrogen, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %. Typically, the hydrogen-lean stream comprises ≥ 25 wt. % of the tail gas's non-aromatic hydrocarbon, e.g., ≥ 50 wt. %.

[0045] Alternatively or in addition to any electric power as may be derived from tail gas combustion (or the combustion of a tail gas component such as molecular hydrogen) in power generator **140**, thermal energy produced by such combustion or a portion thereof can be transferred to aromatizer **124** via thermal conduit **146**. Doing so can, e.g., provide heat for the dehydrocyclization. One or more heat recovery steam generators, including those commonly adapted for gas turbine service, can be used for this purpose. The generated steam can be used as a heat transfer fluid in thermal conduit **146**, for example, for providing heat to aromatizer **124**. Alternatively or additionally, a portion of the separated molecular hydrogen of conduit **144**, or a portion of the tail gas of conduit **130**, or both, may be used to provide heat to aromatizer **124**. For example, one or more of these streams may be combusted in a heater or

chemically reacted in an exothermic reaction that releases heat for the aromatization reaction (or reactor(s)).

[0046] Continuing with reference to Fig. 1, the hydrogen-lean stream can be conveyed via conduit **150** to optional compressor **152**. All or a portion of the compressed hydrogen-lean stream may be used in the process, e.g., for recycling to pretreater **114** via conduits **154** and **112**. This can be desirable when the compressed hydrogen-lean stream has a sufficient C₂₊ non-aromatic hydrocarbon as may be useful for increasing the process's yield of aromatic hydrocarbon. Alternatively or in addition, valve means V₃ and V₄ can be utilized for diverting all or a portion of the hydrogen-lean stream away from the process, e.g., for one or more of storage, further processing, transportation, sales, reservoir reinjection, etc.

[0047] The block diagram of Fig. 1 should not be interpreted as indicating that the system 100 is to include all of the components shown. Certain related aspects within the broader scope of the invention are not shown in Fig. 1. For example, although it is typically not desirable to do so, it is within the scope of the invention to combust in one or more flares all or a portion of the streams of conduits **150** or **154**, e.g., during process upsets. Other aspects which are not shown in Fig. 1 do not include the optional pretreater. These aspects typically utilize a hydrocarbon source that is capable of providing an aromatization feed with the specified preselected volumetric flow rate and the specified preselected concentration of C₂₊ non-aromatic hydrocarbon.

[0048] Part or all of the system **100** may be constructed as a modular system that may be quickly moved and set up at a location, used, then broken down and moved to a new location when no longer needed.

[0049] Certain gaseous feeds that are suitable for producing the specified aromatization feed will now be described in more detail. The invention is not limited to these gaseous feeds, and this description is not meant to foreclose the use of other gaseous feeds within the broader scope of the invention.

Gaseous Feeds

[0050] The gaseous feed, which in aspects illustrated in Fig. 1 is generally introduced into pretreater **114** via conduit **118**, typically includes one or more C₂ to C₉ non-aromatic hydrocarbon compounds, e.g., one or more light hydrocarbon (i.e., C₂ to C₅) compounds, such as one or more paraffinic light hydrocarbon compounds. For example, the gaseous feed **118** can include ≥ 1 wt. % based on the weight of the gaseous feed **118** of one or more of (i)

paraffinic C₂ to C₉ hydrocarbon, (ii) aliphatic C₂ to C₉ hydrocarbon, (iii) aliphatic paraffinic C₂ to C₉ hydrocarbon, (iv) paraffinic light hydrocarbon, (v) aliphatic light hydrocarbon, and (vi) aliphatic paraffinic light hydrocarbon; such as ≥ 10 wt. %, or ≥ 25 wt. %, or ≥ 50 wt. %, or ≥ 75 wt. %, or ≥ 90 wt. %, or ≥ 95 wt. %. Optionally, the gaseous feed further includes diluent.

5 Diluent, when present, is typically included in the gaseous feed in an amount ≤ 60 wt. % based on the weight of the gaseous feed **118**, e.g., ≤ 50 wt. %, such as ≤ 40 wt. %, or ≤ 30 wt. %, or ≤ 20 wt. %, or ≤ 10 wt. %. A feed constituent is diluent when it is substantially non-reactive under the specified reaction conditions in the presence of the specified dehydrocyclization catalyst, e.g., methane, molecular nitrogen, and inert atomic gasses such as argon.

10 **[0051]** The gaseous feed typically contains C₃ and/or C₄ hydrocarbon e.g., (i) ≥ 10 wt. % propane, such as ≥ 40 wt. %, or ≥ 60 wt. %, and/or (ii) ≥ 5 wt. % butanes, such as ≥ 40 wt. %, or ≥ 60 wt. %. Although the gaseous feed can contain C₅₊ hydrocarbon, the amount of C₅₊ hydrocarbon when present is typically small, e.g., ≤ 30 wt. %, such as ≤ 10 wt. %, or ≤ 01 wt. %. Typically, the gaseous feed contains ≤ 15 wt. % of C₆₊ saturated hydrocarbon, e.g., ≤ 5 wt. %.

[0052] The gaseous feed can contain methane, e.g., ≥ 1 wt. % methane, such as ≥ 10 wt. %, or ≥ 20 wt. %, or ≥ 60 wt. %. Even though methane is a diluent, i.e., it typically does not react to produce aromatic hydrocarbon or catalyst coke in the presence of the specified dehydrocyclization catalyst under the specified reaction conditions, its presence is beneficial.

20 It is believed that this benefit results at least in part from a decrease in the partial pressure of the C₂ – C₉ hydrocarbon compounds that is achieved when the gaseous feed further includes methane. Decreasing the partial pressure of the C₂ – C₉ hydrocarbons, particularly the partial pressure of the C₂ – C₅ hydrocarbon, has been found to lessen the amount of catalyst coke formed under the specified dehydrocyclization process conditions. Typically, the gaseous feed

25 includes a total of ≤ 10 wt.% of impurities such as CO, CO₂, H₂S, and total mercaptan; e.g., ≤ 1 wt. %, or ≤ 0.1 wt.%. Although not typically found in gaseous feeds separated from raw natural gas, certain gaseous feeds include molecular hydrogen, e.g., ≥ 1 wt. % molecular hydrogen based on the weight of the gaseous feed **118**, such as ≥ 5 wt. %.

[0053] The gaseous feed includes ethane, typically in an ≥ 1 wt. %, based on the weight of the gaseous feed, e.g., ≥ 5 wt. %, or ≥ 10 wt. %, such as in the range of from 10 wt. % to 40 wt. %. Suitable gaseous feed include those containing a major amount of ethane that is > 50 wt. %, such as ≥ 75 wt. %, or ≥ 90 wt. %, or ≥ 95 wt. %. One representative gaseous feed includes (i) ≥ 10 wt. % ethane, such as in the range of from 10 wt. % to 40 wt. %; and further

includes (ii) 1 wt. % to 40 wt. % methane, (iii) 20 wt. % to 50 wt. % propane, and (iv) 20 wt. % to 50 wt. % butanes. In other aspects, the amount of ethane in the gaseous feed is < 1 wt. %, e.g., ≤ 0.1 wt. %, or ≤ 0.1 wt. %.

[0054] Although the gaseous feed can contain unsaturated C_{2+} hydrocarbon, such as $C_2 - C_5$ unsaturated hydrocarbon, the amount of these unsaturated compounds is typically ≤ 20 wt. %, e.g., ≤ 10 wt. %, such as ≤ 1 wt. %, or ≤ 0.1 wt. %, or in the range of from 0.1 wt. % to 10 wt. %. The gaseous feed **118** can be substantially-free of non-aliphatic hydrocarbon. More particularly, the gaseous feed **118** can be substantially-free of aromatic hydrocarbon, where substantially-free in this context means < 1 wt. % based on the weight of the gaseous feed **118**, such as ≤ 0.1 wt. %, or ≤ 0.01 wt. %, or ≤ 0.001 wt. %.

[0055] In certain aspects, the source of the gaseous feed includes natural gas, e.g., raw natural gas (“raw gas”). Natural gas is (i) a mixture including hydrocarbon, (ii) primarily in the vapor phase at a temperature of 15.6 °C and a pressure of 1.016 bar (absolute), and (iii) withdrawn from a geologic formation. Natural gas can be obtained, e.g., from one or more of petroleum deposits, coal deposits, and shale deposits. One suitable raw natural gas includes 3 mole % to 70 mole % methane, 10 mole % to 50 mole % ethane, 10 mole % to 40 mole % propane, and 5 mole % to 40 mole % butanes and 1 mole % to 10 mole % of total C_5 to C_9 hydrocarbon. In certain aspects, ≥ 50 wt. % of the gaseous feed includes natural gas, such as raw natural gas, e.g., ≥ 75 wt. %, or ≥ 90 wt. %, or ≥ 95 wt. %.

[0056] As described with respect to Fig. 1, all or a portion of the gaseous feed may be an output stream from a gas-liquid separator **104** that separates a gaseous overhead stream (in conduit **116**) from hydrocarbon source **102**. Any form of hydrocarbon source can be used as the feed **102**, so long as it contains sufficient C_{2+} non-aromatic hydrocarbon for producing the gaseous feed and the aromatization feed. For example, hydrocarbon source **102** may include hydrocarbon obtained from field processing units, refineries, chemical plants, and the like.

[0057] In certain aspects, the gaseous feed includes one or more of (i) gas obtained from a natural gas well (“Gas Well”, Non-associated”, or “Dry” gas), (ii) natural gas obtained from a condensate well (“Condensate Well Gas”), and (iii) casing head gas (“Wet” or “Associated” gas). For example, Associated Gas can comprise 0 mole % to 95 mole % of methane, 5 mole % to 50 mole % of ethane, 2 mole % to 40 mole % of propane, 0.1 mole % to 30 mole % of i-butane, 1 mole % to 30 mole % of n-butane, and 0.05 mole % to 25 mole % of i-pentane. Table 1 includes typical raw gas compositional ranges (mole %) and, parenthetically, typical average composition (mole %) of certain raw gases that may be found in these streams.

Table 1: Examples of Feed Compositions

	Associated Gas	Dry Gas	Condensate Well Gas
Component			
CO ₂	0 - 50 (0.63)	0 - 25 (0)	0 - 25 (0)
N ₂	0 - 50 (3.73)	0 - 25 (1.25)	0 - 25 (0.53)
H ₂ S	0 - 5 (0.57)	0 - 5 (0)	0 - 5 (0)
CH ₄	0 - 80 (64.48)	0 - 97 (91.01)	0 - 98 (94.87)
C ₂ H ₆	5 - 20 (11.98)	2 - 10 (4.88)	1 - 5 (2.89)
C ₃ H ₈	2 - 10 (8.75)	0.5 - 5 (1.69)	0.1 - 5 (0.92)
i-butane	0.1 - 5 (0.93)	0.05 - 1 (0.14)	0.1 - 5 (0.31)
n-butane	1 - 5 (2.91)	0.05 - 2 (0.52)	0.05 - 2 (0.22)
i-pentane	0.05 - 2 (0.54)	0.01 - 1 (0.09)	0.1 - 1 (0.09)

[0058] One suitable gaseous feed includes ≥ 75 wt. % Associated Gas, based on the weight of the gaseous feed, e.g., ≥ 90 wt. %, or ≥ 95 wt. %. In conventional petroleum production, the lack of effective natural transportation facilities, e.g., the lack of natural gas liquefaction and/or pipeline facilities, can result in Associated Gas being stranded at or near the reservoir. The stranded Associated Gas may be uneconomical to transport, and, thus, may be flared, which is undesirable. Moreover, even in locations where pipeline facilities are available, Associated Gas may be excluded from the pipeline because it typically exceeds one or more pipeline specifications, e.g., ≤ 12 wt. % ethane, ≤ 5 wt. % propane, ≤ 2 wt. % butanes, a Wobbe Index of from 49.01 MJ/sm³ to 52.22 MJ/sm³, and a heating value of from 36.07 MJ/sm³ to 41.40 MJ/sm³.

[0059] Since methane is not detrimental to the process, and is in at least some aspects beneficial, the techniques described herein can at least partially obviate the need for costly and inefficient cryogenic methane separation facilities. Typically, obtaining the gaseous feed from the hydrocarbon source does not include (i) exposing the gaseous feed, the hydrocarbon source, or any intermediate thereof to a temperature ≤ -37 °C, e.g., ≤ -46 °C, such as ≤ -60 °C. Certain aspects of the techniques do not include cryogenic processing, e.g., cryogenic methane separation is not used.

[0060] The techniques are therefore particularly advantageous in remote or under-developed locations, where (i) the lack of cryogenic methane separation facilities limits the utility of conventional natural gas aromatization processes, (ii) the lack of a pipeline or natural gas production infrastructure, may result in significant quantities of light hydrocarbon being flared or burned as fuel, and (iii) Associated Gas remains stranded at a remote location for lack of pipeline facilities or a failure to meet one or more specifications of an available pipeline.

Gaseous Feed Pretreatment

[0061] The gaseous feed is pretreated to produce the specified aromatization feed. Certain forms of pretreatment, illustrated schematically in Fig. 2, will now be described in more detail. The invention is not limited to these aspects, and this description is not meant to foreclose other forms of pretreatment within the broader scope of the invention, such as those using fractional distillation. Features shown in Fig. 2 which perform substantially the same function as those of Fig. 1 are identified by the same index number.

[0062] Pretreater **114** utilizes gaseous feed provided via conduit **118** to produce a aromatization feed for aromatizer **124** at a preselected amount ≥ 1 MSCFD (29,000 NM³D), e.g., ≥ 10 MSCFD (290,000 NM³D), such as in the range of from 2 MSCFD (57,000 NM³D) to 80 MSCFD ($2.3 \cdot 10^6$ NM³D), or in the range of from 10 MSCFD (290,000 NM³D) to 30 MSCFD (860,000 NM³D). The aromatization feed has a preselected C₂₊ non-aromatic hydrocarbon concentration in the range of from 15 mole % to 90 mole % per mole of aromatization feed, typically 55 mole % to 80 mole %. Typically, the gaseous feed is provided to the pretreater in an amount in the range of from 10 MSCFD (290,000 NM³D) to 150 MSCFD ($4.3 \cdot 10^6$ NM³D).

[0063] In the aspects illustrated in Fig. 2, the pretreating includes (i) transferring heat away from the gaseous feed in at least a first heat transfer stage **201** in order to partially condense the gaseous feed at a predetermined dew point. An overhead stream is separated from the partially condensed gaseous feed in separator drum **203**, the overhead stream being conducted away via conduit **115**. The overhead stream generally has characteristics that place it within established specifications for many gas pipelines, e.g., ≤ 12 wt. % ethane, ≤ 5 wt. % propane, ≤ 2 wt. % butanes, a Wobbe Index of from 49.01 MJ/sm³ to 52.22 MJ/sm³, and a heating value of from 36.07 MJ/sm³ to 41.40 MJ/sm³.

[0064] The aromatization feed is conducted away from separator drum **203** as a bottoms stream via conduit **120**. In order to provide an aromatization feed to aromatizer **124** having the

specified preselected C₂₊ non-aromatic hydrocarbon concentration and the specified preselected volumetric flow rate, the separation in drum **203** is typically carried out at a predetermined dew point in the range of from – 40 °F (-40 °C) to –20 °F (-28.9 °C), typically at a pressure in the range of from about 300 psia (2068 kPa) to about 2000 psia (13,800 kPa),
5 e.g., 400 psia (2760 kPa) to 700 psia (4830 kPa).

[0065] In the aspects shown in Fig. 2, the first heat transfer stage includes at least one heat exchanger in indirect thermal contact with a flow of refrigerant circulating in conduit **204**. The refrigerant can include propane, for example. A second heat transfer stage **202** is used for withdrawing heat from the refrigerant. Typically, second heat transfer stage includes at least
10 one heat exchanger and at least one refrigerant compressor. The refrigerant compressor can be powered by shaft power obtained from the gas turbine of power generator **140** (shown in Fig. 1), for example. Typically, the heat exchanger of heat transfer stage **202** indirectly transfers heat from the refrigerant to at least one heat transfer fluid (not shown), which is conducted away.

15 [0066] In certain aspects, not shown in Fig. 2, the first heat transfer stage **201** indirectly transfers first, second, and third portions of the total quantity of heat transferred from the gaseous feed. The first portion is transferred to the refrigerant and the second portion is transferred to the separated gaseous hydrocarbon. The third portion is transferred to the bottoms stream of separator drum **203**, which at least partially vaporizes the bottoms stream to
20 provide the aromatization feed of conduit **120** in gaseous form. These aspects are particularly efficient. Power is needed (typically provided by at least the refrigerant compressor) for removing heat from the circulating refrigerant in the second heat transfer stage. Most of this power is consumed in condensing the gaseous feed into the bottoms stream, but some power is consumed cooling the gaseous overhead stream, which is conducted away via conduit **115**.
25 Indirectly transferring heat from the gaseous overhead stream to the refrigerant in the first heat transfer stage decreases the refrigerant compressor's power requirements. Advantageously, it has been found that this configuration decreases or eliminates variations in refrigerant compressor power requirements as would otherwise be observed when operating the process using a first gaseous feed from a first geographic location and a second gaseous feed in a second
30 geographic location, the first and second gaseous feeds having a different molar ratio ("M") of C₂ hydrocarbon to C₃₊ non-aromatic hydrocarbon. For gaseous feeds of greater M, the amount of refrigerant compressor power utilized for cooling the gaseous overhead stream is comparatively larger than for those of lesser M. Consequently, transferring heat in the first

heat transfer stage from the gaseous overhead stream to the refrigerant automatically compensates for refrigerant compressor power that would otherwise be needed or surplused in response to a change of gaseous feed.

[0067] When operating in accordance with these aspects, the quantity of heat transferred from the gaseous feed to the refrigerant in the first heat transfer stage typically varies by no more than $\pm 50\%$ (substantially equivalent to a compressor power variation of no more than $\pm 50\%$) over a very wide variety of gaseous feeds obtained from a very wide variety of hydrocarbon sources. Typically, this variation is achieved when the condensed portion of the gaseous feed has a volume variation of $\leq \pm 25\%$, e.g., $\leq \pm 10\%$, or $\pm 5\%$. Further decreases in this variation can be achieved, e.g., no more than $\pm 40\%$, such as no more than $\pm 30\%$, provided (A) the preselected amount of aromatization feed is in the range of from 5 MSCFD (140,000 NM³D) to 35 MSCFD ($1 \cdot 10^6$ NM³D), (B) the amount gaseous feed is in the range of from 30 MSCFD (860,000 NM³D) to 140 MSCFD ($4 \cdot 10^6$ NM³D), and (C) the gaseous feed has a molar ratio of C₂ hydrocarbon to C₃₊ non-aromatic hydrocarbon in the range of from 0.5 to 1.5. This effect is a significant advantage in standardization of pretreater refrigeration capacity, e.g., since modularization is less difficult to achieve when pretreater refrigeration capacity is substantially independent of the choice of gaseous feed.

[0068] In certain aspects, the pretreatment is configured to advantageously decrease variations recoverer capacity as might otherwise be needed when changing from the first gaseous feed to the second gaseous feed. Fewer aromatic hydrocarbon compounds are produced (molar basis) by dehydrocyclization of the aromatization feed's C₂ hydrocarbon than are produced by dehydrocyclization of the aromatization feed's C₃₊ non-aromatic hydrocarbon. Consequently, gaseous feeds having a greater value of M will need a recoverer of comparatively lesser capacity than for those having a lesser value of M. It has been found that this effect can be at least partially overcome by operating the pretreatment to produce an aromatization feed having a preselected concentration of C₃₊ hydrocarbon within a relatively narrow range. For example, it has been observed that when the aromatization feed comprises C₂ hydrocarbon in an amount in the range of from 10 mole % to 35 mole % and C₃₊ hydrocarbon in an amount in the range of from 40 mole % to 50 mole %, that the first product is recovered in an amount that varies by no more than $\pm 25\%$. Further decreases in this variation can be achieved, e.g., no more than $\pm 20\%$, such as no more than $\pm 15\%$, when (A) the preselected amount of aromatization feed is in the range of from 5 MSCFD (140,000 NM³D) to 35 MSCFD ($1 \cdot 10^6$ NM³D), (B) the amount of gaseous feed is in the range of from

30 MSCFD (860,000 NM³D) to 140 MSCFD (4•10⁶ NM³D), and (C) the gaseous feed has a molar ratio of C₂ hydrocarbon to C₃₊ non-aromatic hydrocarbon in the range of from 0.5 to 1.5. This effect is a significant advantage in standardization of recoverer capacity, e.g., since modularization is less difficult to achieve when the recoverer capacity is substantially independent of the choice of gaseous feed.

[0069] The feed pretreater **114** may be constructed onto a first set of modules, wherein the division of the units into the separate modules is based on the amount of flow. For example, the separator drum **203**, and supporting units, may be constructed into a single skid for small scale applications, e.g., less than about 10 million standard cubic feet per day (MSCFD) (290,000 NM³D), less than about 5 MSCFD (140,000 NM³D), or less than about 1 MSCFD (29,000 NM³D).

[0070] For larger applications, e.g., greater than about 20 MSCFD (570,000 NM³D), greater than about 35 MSCFD (1•10⁶ NM³D), or greater than about 50 MSCFD (1.4•10⁶ NM³D), first heat transfer stage **201**, second heat transfer stage **202**, and separator drum **203** may be separated among two or more modules. A typical skid has a gross weight ≤ 200,000 pounds (91,000 kg), e.g., ≤ 80,000 pounds (36,300 kg), such as in the range of from 10,000 pounds (4500 kg) to 200,000 pounds (91,000 kg), or 50,000 pounds (22,700 kg) to 150,000 pounds (68,000 kg); a width ≤ 15 feet (4.6 m), e.g., ≤ 102 inches (2.6 m); and a height ≤ 15 feet (4.6 m), e.g., ≤ 14.6 feet (4.45 m). Those skilled in the art will appreciate that these arrangements are only one example, and any number of different arrangements and systems as may be used for the feed pretreater **114**.

Aromatizer

[0071] Certain forms of aromatizer **124** will now be described in more detail with reference to Fig. 2. The invention is not limited to these forms of aromatizer, and this description is not meant to foreclose other forms of aromatizers within the broader scope of the invention. Aromatizer **124** may be contained in a single module, or alternatively distributed over a plurality of modules, e.g., to accommodate the reactors and associated equipment. In the aspects shown in Fig. 2, a single reactor **224** is used. The aromatization feed of conduit **120** may be heated to reactor temperatures by flowing through a number of heat exchangers, **226**, **228**, **236**, e.g., for exchanging heat with the reaction effluent **126**. To achieve the final temperatures used to maintain an endothermic dehydrocyclization reaction, the reactor feed of conduit **120** may pass through heater **230**. Heater **230** may derive heat from hot flue gas conducted via conduit **146**, such as hot flue gas produced by combustion in turbo-machinery

of power generator **140**. Alternatively or in addition (e.g., during start-up) the heater may be one which utilizes combustion. A portion of the tail gas in conduit **130** can be conducted to the heater to provide fuel for the combustion, at least until start-up has progressed sufficiently for the transfer of hot flue gas from power generator **140** to the heater via conduit **146**. Heater **230** may also be used to heat a circulation stream **232** from the reactor **224** to maintain reactor temperatures. It is understood that the fired heater **230** may include one or more heat recovery units (HRU) associated with a flue gas from a power generator **140**, e.g., one or more heat recovery steam generators. An optional hot oil stream can be circulated via conduit **234** to provide heat to components of system **100** and/or to other systems.

10 **[0072]** The reactor **224** uses a dehydrocyclization process to convert to aromatic hydrocarbon at least a portion of the aromatization feed's C₂₊ non-aromatic hydrocarbon. In this form of dehydrocyclization, the aromatization feed obtained from conduit **120** is heated in heat transfer stages **226** and **228** by transferring heat from the reaction effluent of conduit **126** to the aromatization feed. The heated aromatization feed is reacted in the presence of a
15 catalytically effective amount of at least one dehydrocyclization catalyst located in at least one reaction zone operating under catalytic dehydrocyclization conditions. The reaction converts at least a portion of the aromatization feed's C₂ – C₉ non-aromatic hydrocarbon to aromatic hydrocarbon and molecular hydrogen. Typically, the dehydrocyclization catalyst includes $\geq$ 10 wt. % of a molecular sieve component and $\geq$ 0.005 wt. % of a dehydrogenation component.

20 **[0073]** When the molecular sieve component and dehydrogenation component together include less than 100 wt. % of the catalyst, $\geq$ 90 wt. % of the remainder of the catalyst can include a matrix component, such as $\geq$ 99 wt. % of the remainder. The catalyst typically includes the molecular sieve component in an amount $\geq$ 20 wt. %, based on the weight of the catalyst, e.g., $\geq$ 25 wt. %, such as in the range of from 30 wt. % to 99.9 wt. %. In certain
25 aspects, the molecular sieve component includes aluminosilicate, e.g., $\geq$ 90 wt. % of at least one aluminosilicate. The aluminosilicate can be an un-substituted aluminosilicate, a substituted aluminosilicate, or a combination thereof. For example, the aluminosilicate can be in a form where at least a portion of its original metal has been replaced, e.g., by ion exchange, with other suitable metal (typically metal cation) of Groups 1-13 of the Periodic Table. Typically, the
30 aluminosilicate includes zeolite aluminosilicate, e.g., $\geq$ 90 wt. % of at least one zeolite based on the weight of the aluminosilicate. The term zeolite includes those in which at least part of the aluminum is replaced by a different trivalent metal, such as gallium or indium.

[0074] The molecular sieve component typically includes $\geq$ 90 wt. % of one or more of the

specified molecular sieves, e.g., ≥ 95 wt. %. In certain aspects, the molecular sieve component includes at least one zeolite molecular sieve, e.g., ≥ 90 wt. % zeolite, such as ≥ 95 wt. %, based on the weight of the molecular sieve component. Although, the molecular sieve component can consist essentially of or even consist of zeolite, in alternative aspects the zeolite(s) is present in the molecular sieve component in combination with other (e.g., non-zeolitic) molecular sieve. The zeolite can be one that is in hydrogen form, e.g., one that has been synthesized in the alkali metal form, but is then converted from the alkali to the hydrogen form. Typically the zeolite is one having a medium pore size and a Constraint Index of 2-12 (as defined in U.S. Patent No. 4,016,218). Examples of suitable zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, and ZSM-48, including and mixtures and intermediates thereof such as ZSM-5/ZSM-11 admixture. Optionally, the zeolite is one including at least one set of pores of substantially uniform size extending through the molecular sieve, wherein geometric mean of the cross-sectional dimensions of each of the sets of pores is > 5 Å, or > 5.3 Å, e.g., ≥ 5.4 Å such as ≥ 5.5 Å, or in the range of 5 Å to 7 Å, or 5.4 Å to 7 Å. ZSM-5 and/or ZSM-12 are suitable, particularly H-ZSM-5. For example, the molecular sieve component can include ≥ 90 wt. % of (A) ZSM-5 and/or (B) ZSM-12, based on the weight of the molecular sieve component, e.g., ≥ 95 wt. % of H-ZSM-5. In certain aspects, the molecular sieve has a relatively small crystal size, e.g., small crystal ZSM-5, meaning ZSM-5 having a crystal size ≤ 0.05 micrometers (μm), such as in the range of 0.02 μm to 0.05 μm . Small crystal ZSM-5 and the method for determining molecular sieve crystal size are disclosed in U.S. Patent No. 6,670,517, which is incorporated by reference herein in its entirety.

[0075] In other aspects, the molecular sieve component includes at least one molecular sieve of the MCM-22 family, e.g., MCM-22 alone or in combination with other molecular sieve such as one or more of the specified zeolites. The MCM-22 family includes those molecular sieves having an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstrom. The X-ray diffraction data used to characterize the material are obtained by standard techniques using the K-alpha doublet of copper as incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system. Examples of suitable MCM-22-family molecular sieve is described in U.S. Patents Nos. 4,954,325; 4,439,409 (PSH-3); 4,826,667 (SSZ-25); 6,077,498 (ITQ-1); 5,250,277 (MCM-36); 5,236,575 (MCM-49); and 5,362,697 (MCM-56). Others include UZM-8, ERB-1, as described in European Patent No. 0293032, and ITQ-2, as described in International Patent Publication No. WO 97/17290. Mixtures of MCM-22-family molecular sieve can be used as well.

[0076] When the molecular sieve component includes at least one aluminosilicate, the aluminosilicate's silica : alumina ratio (substantially the same as the aluminosilicate's Si : Al₂ atomic ratio) is typically ≥ 2 , e.g., in the range of from 5 to 100. The silica : alumina ratio is meant to represent the Si : Al₂ atomic ratio in the rigid anionic framework of the crystalline aluminosilicate. Alternatively or in addition, the catalyst can be made more resistant to deactivation (and increase aromatic hydrocarbon yield) by including phosphorous with the molecular sieve component. When used, the amount of phosphorous is typically ≥ 1 wt. % based on the weight of the molecular sieve component. For example, when the molecular sieve component includes aluminosilicate, the phosphorous : aluminum atomic ratio can be in the range of from 0.01 to 1. Zeolite having a higher silica : alumina ratio can be utilized when a lower catalyst acidity is desired, e.g., in the range of from 44 to 100, such as from 50 to 80, or 55 to 75.

[0077] In addition to the molecular sieve component, the catalyst includes ≥ 0.005 wt. %, based on the weight of the catalyst, of a dehydrogenation component, e.g., at least one dehydrogenation metal. The dehydrogenation component can include one or more neutral metals selected from Groups 3 to 13 of the Periodic Table, such as one or more of Ga, In, Zn, Cu, Re, Mo, W, La, Fe, Ag, Pt, and Pd, and/or one or more oxides, sulfides and/or carbides of these metals. For example, the dehydrogenation component can be Ga, Zn, or a combination thereof, optionally supported on a catalyst including ZSM-5 as the molecular sieve component.

[0078] Typically, the dehydrogenation component includes ≥ 90 wt. % of the one or more of the specified dehydrogenation metals and/or oxide thereof, e.g., ≥ 95 wt. %, or ≥ 99 wt. %. For example, the dehydrogenation component can include ≥ 90 wt. % of (A) Ga and/or (B) Zn, including oxides thereof. Typically, the catalyst includes ≥ 0.01 wt. % of the dehydrogenation component, based on the weight of the catalyst, e.g., ≥ 0.1 wt. % of the dehydrogenation component, such as ≥ 0.5 wt. %, or ≥ 1 wt. %.

[0079] Those skilled in the art will appreciate that when the dehydrogenation component includes one or more metals of greater catalytic dehydrogenation activity, e.g., Pt, and/or Pd, a lesser amount of dehydrogenation component is needed, e.g., in the range of 0.005 wt. % to 0.1 wt. %, based on the weight of the catalyst, such as 0.01 wt. % to 0.6 wt. %, or 0.01 wt. % to 0.05 wt. %. When the dehydrogenation component includes one or more metals of lesser dehydrogenation activity, e.g., one or more of Ga, In, Zn, Cu, Re, Mo, and W, a greater amount of dehydrogenation component is needed, e.g., in the range of 0.05 wt. % to 10wt. %, based on the weight of the catalyst, such as 0.1 wt. % to 5 wt. %, or 0.5 wt. % to 2 wt. %.

[0080] The dehydrogenation component can be provided on, in, or proximate to the catalyst in any manner, for example by conventional methods such as impregnation or ion exchange. At least part of the dehydrogenation metal may also be present in the crystalline framework of the molecular sieve. For one representative catalyst, (i) the dehydrogenation component
5 includes ≥ 95 wt. % of (A) Ga and/or (B) Zn, and (ii) the first molecular sieve component includes ≥ 95 wt. % of H-ZSM-5.

[0081] In certain aspects, the dehydrogenation component includes ≥ 99 wt. % of one or more of Ga, Zn, and In, and the molecular sieve component includes ≥ 99 wt. % of ZSM-5-type zeolite that has been impregnated with the dehydrogenation metal component and/or ion
10 exchanged with the dehydrogenation metal component. For example, the catalyst can include Ga-impregnated and/or In-impregnated H-ZSM-5, Ga-exchanged and/or In-exchanged H-ZSM-5, H-gallosilicate of ZSM-5 type structure and H-galloaluminosilicate of ZSM-5 type structure. Optionally, the catalyst includes (i) tetrahedral aluminum and/or gallium, which is present in the zeolite framework or lattice, and/or (ii) octahedral gallium or indium, which is
15 not present in the zeolite framework but present in the zeolite channels in close vicinity to the zeolitic protonic acid sites. While not wishing to be bound by any theory or model, the tetrahedral or framework Al and/or Ga is believed to contribute to acid function of the catalyst and octahedral or non-framework Ga and/or In is believed to contribute to the dehydrogenation function of the catalyst. Although typically the zeolite is impregnated or ion-exchanged with
20 the dehydrogenation metal, other forms of zeolite can be used, such as H-galloaluminosilicate of ZSM-5 type structure having framework (tetrahedral) Si/Al and Si/Ga atomic ratios of about 10:1 to 100:1 and 15:1 to 150:1, respectively, and non-framework (octahedral) Ga of about 0.5 wt. % to 0 wt. %.

[0082] Besides the molecular sieve component and dehydrogenation component, the
25 catalyst can further include an optional matrix component, e.g., one or more inorganic binders. The amount of matrix component is not critical. When present, the amount of matrix component is typically in the range of 0.01 times the weight of the molecular sieve component to about 0.9 times the weight of the molecular sieve component, e.g., in the range of 0.02 to 0.8. The matrix component can include active materials, such as synthetic or naturally occurring zeolites.
30 Alternatively, or in addition, the matrix component can include clays and/or oxides such as alumina, silica, silica-alumina, zirconia, titania, magnesia or mixtures of these and other oxides. The matrix component can include naturally occurring materials and/or materials in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Clays may also be

included with the oxide type binders to modify the mechanical properties of the catalyst or to assist in its manufacture.

[0083] Alternatively or in addition, the matrix component can include one or more substantially inactive materials. Inactive materials suitably serve as diluents to control the amount of conversion so that products may be obtained economically and orderly without
5 employing other means for controlling the rate of reaction. Alternatively or in addition to any phosphorous added to or impregnated into the molecular sieve component, the matrix component can optionally include phosphorous, e.g., to lessen catalyst acidity. Those skilled in the art will appreciate that lessening catalyst acidity decreases the amount of catalyst coke
10 produced during the catalytic conversion of the feed's light hydrocarbon to aromatic hydrocarbon. Suitable phosphorous-containing matrices are disclosed in U.S. Patent No. 5,026,937, which is incorporated by reference herein in its entirety. The matrix component is optional. In certain aspects, the catalyst is substantially-free of matrix, e.g., contains ≤ 1 wt. % of matrix, such as ≤ 0.1 wt. %. In particular, the catalyst can be substantially free of binder,
15 e.g., contains ≤ 1 wt. % of binder, such as ≤ 0.1 wt. %. For example, the catalyst's molecular sieve component can include ≥ 95 wt. % of self-bound bound molecular sieve, e.g., ≥ 95 wt. % of self-bound ZSM-5, and in particular small crystal H-ZSM-5.

[0084] The catalyst can be one that has been subjected to one or more treatments, e.g., a selectivation treatment to increase selectivity for producing desired aromatic hydrocarbon
20 compounds such as para-xylene. For example, the selectivation can be carried out before introduction of the catalyst into the reactor and/or in-situ in the reactor, e.g., by contacting the catalyst with a selectivating agent, such as at least one organosilicon in a liquid carrier and subsequently calcining the catalyst at a temperature of 350 °C to 550 °C. This selectivation procedure can be repeated two or more times and alters the diffusion characteristics of the
25 catalyst such that the formation of para-xylene over other xylene isomers is favored. Such a selectivation process is described in detail in U.S. Patent Nos. 5,633,417 and 5,675,047.

[0085] Typically, the catalyst has a surface area as measured by nitrogen physisorption in the range of from 100 m²/g to 600 m²/g, e.g., in the range of from 200 m²/g to 500 m²/g. When the catalyst includes aluminosilicate which includes phosphorous, the phosphorous : aluminum
30 atomic ratio is typically in the range of from 0.01 to 0.5. For example, the catalyst can contain ≥ 10 wt. % of phosphorous-modified alumina, such as ≥ 15 wt. %, or in the range of from 10 wt. % to 20 wt. %.

[0086] During dehydrocyclization, at least a portion of the C₂₊ non-aromatic hydrocarbon

of the specified aromatization feed of conduit **120** is converted to aromatic hydrocarbon, molecular hydrogen, and optionally additional non-aromatic hydrocarbon. The catalytic dehydrocyclization conditions can include exposing the feed to a temperature in the range of from 400 °C to 650 °C, a pressure in the range of from 100 kPa to 2200 kPa. Typically, the catalytic dehydrocyclization conditions further include a weight hourly space velocity (WHSV) $\geq 0.1 \text{ hr}^{-1}$. More typically, the catalytic dehydrocyclization conditions include a temperature in the range of from 500 °C to 625 °C, a pressure in the range of from 30 psia (207 kPa) to 80 psia (522kPa). WHSV can be in the range of from 0.1 hr^{-1} to 20 hr^{-1} . Typically, the WHSV of C_{2+} hydrocarbon (the “ C_{2+} WHSV”) in the specified aromatization feed with respect to the dehydrocyclization catalyst is in the range of from 0.1 hr^{-1} to 20 hr^{-1} , e.g. 0.2 hr^{-1} 5 hr^{-1} , or 0.3 hr^{-1} to 1 hr^{-1} . The C_{2+} WHSV is the hourly rate of the C_{2+} hydrocarbon (in grams per hour) exposed to the second catalyst per gram of the dehydrocyclization catalyst. The reaction is typically endothermic. Generally, the average temperature drop across the reaction zone is ≤ 600 °C, more typically in the range of from 20 °C to 200 °C, e.g., in the range of from 50 °C to 150 °C.

[0087] The reaction effluent of conduit **126** from reactor **224** may be cooled by exchanging heat with the reactor feed stream of conduit **120** through the heat transfer stages **226** and **228**. Further cooling may be provided by flowing the reaction effluent of conduit **126** through other coolers, e.g., air cooler **236**. The reaction effluent is conducted away from aromatizer **124** via conduit **126** to recoverer **128**, e.g., for recovery of at least a portion of the reaction effluent's aromatics.

[0088] When the aromatizer is operated using the specified aromatization feed under the specified conditions, the dehydrocyclization typically results in (i) ≥ 25 wt. % conversion of the aromatization feed's C_{2+} , e.g., $\geq 25\%$, such as $\geq 50\%$, or $\geq 75\%$; and (ii) a C_{3+} conversion $\geq 50\%$, e.g., $\geq 75\%$, or $\geq 90\%$, or $\geq 95\%$, or $\geq 98\%$. The reaction effluent typically includes (i) unreacted feed, including unconverted diluent, and (ii) vapor-phase and/or liquid-phase products of the dehydrocyclization reaction and other reaction pathways, product phase being that subsisting at the outlet of the downstream-most dehydrocyclization reaction zone of reactor **224**. Typically, the reaction effluent does not include solid (e.g., catalyst coke) and/or semi-solid (e.g., catalyst coke precursors) products of dehydrocyclization and other reaction pathways, as these generally remain in the first stage until they are removed during regeneration mode.

[0089] The reaction effluent typically comprises ≥ 10 wt. % aromatic hydrocarbon,

molecular hydrogen, ≥ 1 wt. % ethane, 1 wt. % to 40 wt. % methane, ≤ 2 wt. % propane, and ≤ 1 wt. % butanes. The amount of ethane in the reaction product can be, e.g., ≥ 5 wt. %, such as ≥ 10 wt. %, particularly when operating the dehydrocyclization at a relatively high temperature within the specified temperature range. Since ethane is typically produced by hydrogenolysis of the aromatization feed's C_{3+} non-aromatic hydrocarbon during the dehydrocyclization, the reaction effluent generally contains ethane and methane even when the aromatization feeds contains < 1 wt. % of ethane and/or < 1 wt. % of methane.

Recoverer

[0090] Certain forms of recoverer **128** are illustrated schematically in Fig. 2. Typically, the recoverer includes at least one separation stage **129** for separating from reaction effluent of conduit **126** at least a tail gas, which is conducted away via conduit **130**, and a first product, which is conducted away via conduit **138**.

[0091] In the aspects illustrated in Fig. 2, separation stage **129** includes at least one separator drum for separating tail gas and first product from the reaction effluent. The invention encompasses recoverers having one or more separation stages, and separation stages having one or more separator drums. Any suitable separation technology can be utilized in separation stage **129**, including conventional separation technology such as membrane separators, distillation columns, etc.

[0092] The first product typically comprises ≥ 50 wt. % of the reaction effluent's aromatic hydrocarbon, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %, or ≥ 95 wt. %. The recovery of the first product from the reaction effluent's aromatic hydrocarbon is typically carried out at a recovery rate in the range of from 200 barrels per day ("BPD") (3.2 M³PD) to 10,000 BPD (160 M³PD), e.g., 500 BPD (7.9 M³PD) to 5000 BPD (79 M³PD), such as 1000 BPD (16 M³PD) to 4000 BPD (64 M³PD). The tail gas typically comprises ethane and molecular hydrogen, and typically further comprises methane. For example, the tail gas can comprise 1 wt. % ethane, e.g., ≥ 5 wt. %, such as ≥ 10 wt. %. In a particular aspect, the tail gas comprises (A) ≥ 75 wt. % of the reaction effluent's ethane, e.g., ≥ 90 wt. %, such as ≥ 95 wt. %; and (B) ≤ 10 wt. % of the reaction product's aromatic hydrocarbon, e.g., ≤ 5 wt. %, such as ≤ 1 wt. %. Typically, the tail gas further comprises (a) ≥ 10 wt. % of the reaction effluent's molecular hydrogen, e.g., ≥ 25 wt. %, such as ≥ 50 wt. %, or ≥ 95 wt. %, and/or ≥ 10 wt. % of the reaction effluent's methane, e.g., ≥ 25 wt. %, such as ≥ 50 wt. %, or ≥ 95 wt. %.

Optional Second Dehydrocyclization Stage

[0093] The aromatization of the aromatization feed is not limited to a single reactor zone, or a single reactor, or a single reaction stage. Dividing the reaction among multiple zones and/or reactors may allow for more efficient production of the cyclic products, for example, with higher yields and longer periods before coking. Further, dividing the reactor among multiple zones and multiple vessels lessens the difficulties associated with construction of a higher throughput module system, for example, having a throughput of 50 MSCFD ($1.4 \cdot 10^6$ NM³D) or greater.

[0094] Certain aspects of the invention which include an aromatizer having first and second reaction stages are illustrated schematically in Fig. 3. Features of Fig. 3 which perform substantially the same function as those of Fig. 1 and Fig. 2 are identified by the same index number. Although the two reaction stages may be part of a single reactor vessel or in separate vessels for each stage, the aspects of Fig. 3 include a second reaction stage having a reactor **334** that is distinct from reactor **224** of the first reaction stage. The total selectivity for one or more of (i) additional methane, (ii) additional ethane, and (iii) additional C₃₊ light hydrocarbon in stages 1 and 2 has been found to be less than would be the case if stages 1 and 2 were combined into a single stage operating under conditions specified for either stage 1 or stage 2. Typically, for an aromatization feed which includes Associated Gas, the aromatization (e.g., stages 1 and 2 operating together) exhibits (i) a total conversion of C₂-C₄ hydrocarbon $\geq 30\%$, e.g., $\geq 40\%$, such as $\geq 50\%$, and (ii) a selectivity for aromatic hydrocarbon $\geq 30\%$, e.g., $\geq 40\%$, such as $\geq 50\%$. Desirably, this performance can be achieved in a single pass.

[0095] As shown in Fig. 3, the tail gas in conduit **130A** is heated in heat transfer stages **326**, **336**, and **328**. Additional heat is provided to the tail gas by heater **330**. If desired, a portion of the tail gas's molecular hydrogen can be combusted to provide additional heat. When molecular hydrogen combustion is used, the combustion is typically selective molecular hydrogen combustion. The heated tail gas is introduced into second reactor **334** for dehydrocyclization of at least a portion of the tail gas's C₂₊ non-aromatic hydrocarbon to produce a second reaction effluent comprising additional aromatic hydrocarbon and additional molecular hydrogen, these being "additional" in the sense that they are in addition to those produced in first reactor **224**. Although reactor **334** is shown having two beds of dehydrocyclization catalyst with inter-bed heating provided by heater **330**, the second reactor is not limited to such forms. For example, a portion of the molecular hydrogen produced in the upstream bed of reactor **334** can be combusted to provide additional heat for the

endothermic dehydrocyclization reaction of the downstream bed.

[0096] Heat is transferred away from the second reaction effluent in heat transfer stages 326, 336, and 328, and is conducted via conduit 325 to recoverer 128 for recovery of a second tail gas and a second product. As shown in Fig. 3, this separation can be carried out in a second separation stage associated with recoverer 128. As is the case with the first and second reaction stages, which can be located in individual modules of the aromatizer, the first and second stages of the recoverer can be located in individual modules of the recoverer. This lessens the difficulty of distributing these functions over modules of a standard size that are useful for operations in a variety of geographic locations.

[0097] The aromatizer's second stage typically converts ≥ 5 wt. % of the tail gas's ethane, e.g., ≥ 10 wt. %, such as ≥ 20 wt. %. Since the first product typically contains ≤ 5 wt. % of C_{3+} hydrocarbon, e.g., ≤ 2 wt. % propane, and ≤ 1 wt. % butanes, little if any conversion of C_{3+} hydrocarbon occurs in reactor 334. This effect desirably decreases the accumulation of catalyst coke in stage 2.

[0098] Surprisingly, it has been found that appreciable conversion of the first product's ethane to aromatic hydrocarbon can be achieved with less or substantially no removal of the first reaction effluent's aromatic hydrocarbon upstream of the second stage, even when the reaction temperature of the second stage exceeds that of the first stage. Accordingly, in certain aspects that are not shown in Fig. 3, the recoverer does not utilize first separation stage 129, or utilizes a first separation stage of lesser capacity and/or one using different separation conditions. Although these aspects encompass conducting substantially all of the first reaction effluent to second reactor 334, they also encompass, e.g., configuring separation stage 129 to remove at least a portion of the first reaction effluent's molecular hydrogen (and/or a portion of the of the first reaction effluent's methane) before the remainder of the tail gas is introduced into reactor 334. Methane separation can be desirable when the first reaction effluent would otherwise contain more methane than is needed for lessening the ethane partial pressure reactor 334 into a range which decreases coke accumulation and increases aromatic hydrocarbon yield.

[0099] As an example of such alternative aspects, the feed to reactor 334 can include ≥ 90 wt. % of the reaction effluent of reactor 224, e.g., ≥ 95 wt. %, such as ≥ 99 wt. %. Although little if any compositional separation between reactors 224 and 334 is used in these aspects, it is within their scope to divide the entirety of first reaction effluent into two or more streams, with one stream including ≥ 50 wt. % of the entirety of the first reaction effluent being conducted to reactor 334, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %, or ≥ 95 wt. %; and one or more

additional streams being conducted away from the process. It is also within the scope of these aspects to separate at least a portion of the first reaction effluent's aromatic hydrocarbon upstream of reactor **334**. However, in these aspects the portion of the first reaction effluent that is reacted under dehydrocyclization conditions in reactor **334** typically includes ≥ 50 wt. % of the first reaction effluent's aromatic hydrocarbon, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %, or ≥ 95 wt. %; and ≥ 50 wt. % of the first reaction effluent's molecular hydrogen, such as ≥ 90 wt. %, or ≥ 95 wt. % . Also typical of these aspects is that the portion of the first reaction effluent that is reacted under dehydrocyclization conditions in reactor **334** includes ≥ 50 wt. % of the first reaction effluent's ethane, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %, or ≥ 95 wt. %; and ≥ 50 wt. % of any other (i.e., besides ethane) non-aromatic hydrocarbon in the first reaction effluent, e.g., ≥ 75 wt. %, such as ≥ 90 wt. %, or ≥ 95 wt. % . The inter-stage separations of these aspects, when used, are typically carried out in separation stage **129** of recoverer **128**. Alternatively or in addition to the aspects illustrated in Fig. 2, and Fig. 3, heat can be provided for the dehydrocyclization reaction of reactors **224** and/or **334** by techniques other than fired heaters. For example, in certain aspects, at least a portion of the heat is provided by (i) electric heating, which can utilize electric power produced in power generator **140** and/or (ii) a hot oil system or steam system that recovers heat in a heat recovery unit from a flue gas emitted by a gas turbine of power generator **140**. In these or other aspects, at least a portion of the heat is provided by combusting at least a portion of the molecular hydrogen produced in the upstream and downstream catalyst beds. Oxidant for the combustion can be introduced into the reactors, e.g., at one or more of the following locations: at the upstream catalyst bed, (ii) at the downstream catalyst bed, between the upstream and downstream catalyst beds, downstream of the downstream catalyst bed. Typically, the molecular hydrogen combustion, when used, is selective molecular hydrogen combustion ("SHC"), e.g., selectively combusting molecular hydrogen instead of hydrocarbon. The SHC can be catalytic SHC, e.g., with the SHC catalyst located proximate to the dehydrocyclization catalyst. Suitable molecular hydrogen combustion schemes are disclosed in U.S. Patent No. 5,026,937, which is incorporated by reference herein in its entirety. Oxidant for the molecular hydrogen combustion or selective molecular hydrogen combustion can be, e.g., air and/or molecular oxygen, including molecular oxygen in air. Alternatively or in addition, oxidant can be provided by one or more solid carriers of oxygen (solid oxygen carries, or "SOC"), which can be replenished with oxidant when the aromatizer is in regeneration mode. In certain aspects, the SOC is composited with the SHC. It has been observed that decreasing the amount of molecular hydrogen in the reactors increases the yield of aromatic hydrocarbon. It has also been observed that it is typically not desirable

to combust substantially all of the molecular hydrogen in reactors, but only sufficient molecular hydrogen combustion to provide the heat needed for the endothermic dehydrocyclization. It has been found that a long cycle time is easier to achieve when at least some molecular hydrogen is present in the reactors.

5 [0100] Although dehydrocyclization process conditions in reactor 334 can be the same as those of reactor 224, typically they are different. Similarly, although the same dehydrocyclization catalyst can be utilized in reactors 224 and 334, typically they are different. Although Figs. 2 and 3 show reactors 224 and 334 as having two catalyst beds (an upstream bed and a downstream bed), the invention is not limited reactors of this form. Reactors having
10 one catalyst bed are within the scope of the invention, as are reactors having three or more beds. Reactors having moving catalyst beds and/or fluidized catalyst beds are within the scope of the invention, although typically reactors 224 and 334 each contain at least one fixed catalyst bed. In the aspects illustrated in Fig. 3, each of the first and second reaction stages include one reactor (224 and 334). The invention, however, is not limited to reaction stages having one
15 reactor, and in other aspects additional reactors are used, e.g., for additional dehydrocyclization. Aromatizer 124 can include more than two reaction stages. The stages can each have the same number of reactors, but this is not required. In certain aspects using an aromatizer having two reaction stages (as in those aspects illustrated in Fig. 3), the catalytic dehydrocyclization conditions in reactor 224 include exposing the aromatization feed to a
20 temperature T_1 in the range of from 400 °C to 630 °C, and a pressure P_1 that is sufficient for carrying out the dehydrocyclization. Typically, T_1 is in the range of from 450 °C to 605 °C. Typically, P_1 is ≥ 20 psia (137.9 kPa) e.g., ≥ 35 psia (241.3 kPa), such as in the range of from 35 psia (241.3 kPa) to 300 psia (2070 kPa). For example, P_1 can be in the range of from 35 psia (241.3 kPa) to 300 psia (2070 kPa), such as 37 psia (255.1 kPa) to 80 psia (522 kPa), or
25 40 psia (275.8 kPa) to 80 psia (522kPa), or 45 psia (310.2 kPa) to 80 psia (522kPa). Generally, the catalytic dehydrocyclization conditions further include a weight hourly space velocity (WHSV) in the range of from 0.1 hr^{-1} to 20 hr^{-1} , e.g., 0.2 hr^{-1} to 5 hr^{-1} , such as 0.3 hr^{-1} -to 1.0 hr^{-1} . WHSV is based on the aromatization feed's C_{2+} hydrocarbon content, and is the hourly rate of the aromatization feed's C_{2+} hydrocarbon (in grams) per gram of the first catalyst. In a
30 particular aspect, (i) the average temperature across any reaction zone within reactor 224 (and across any catalyst bed located within a reaction zone of reactor 224) is ≤ 600 °C; and (ii) the aromatization feed is not exposed to a temperature ≥ 630 °C at the inlet to reactor 224. Typically, the dehydrocyclization reaction of reactor 224 is carried out at a relatively large pressure (relative to the pressure of reactor 334), so hydrogen is produced by the

dehydrocyclization reaction at a relatively large partial pressure. It was expected that the large partial pressure of hydrogen would suppress feed dehydrogenation, leading to a decrease in the yield of C₆₊ hydrocarbon such as aromatic hydrocarbon. Surprisingly this has been found to not be the case: the relatively large hydrogen partial pressure in reactor **224** has been found to

5 lessen the rate of catalyst coke accumulation with little or no decrease in the yield of aromatic hydrocarbon. For example, when the dehydrocyclization conditions in reactor **224** include a pressure $P_1 \geq 35$ psia (241.3 kPa, the dehydrocyclization reaction can be sustained for a time duration ≥ 50 hours, e.g., ≥ 100 hours, such as ≥ 200 hours, or ≥ 500 hours with a decrease in the yield of aromatic hydrocarbon of $\leq 10\%$, e.g., $\leq 5\%$, such as $\leq 1\%$.

- 10 **[0101]** Those skilled in the art will appreciate that within the ranges of process parameters specified for the reactor **224**, there are process conditions which if selected would result in a maximum propane conversion to aromatic hydrocarbon “X_{MP}”. Unlike conventional multi-stage processes, reactor **224** is typically operated at a propane conversion to aromatic hydrocarbon that is less than X_{MP}. Instead, when the aromatization feed includes propane
- 15 and/or when propane is produced in reactor **224**, process conditions are generally selected so that the initial (start of run) propane conversion to aromatic hydrocarbon in reactor **224** “X_{IP}” is $\leq 0.95 \cdot X_{MP}$. Typically, $X_{IP} \leq 0.90 \cdot X_{MP}$, e.g., $\leq 0.85 \cdot X_{MP}$, or $\leq 0.80 \cdot X_{MP}$, or $\leq 0.75 \cdot X_{MP}$. It has been found that operating reactor **224** under conditions which provide $X_{IP} \geq X_{MP}$ lead to excessive catalyst coking, typically resulting in a shortened cycle time in fixed bed operation.
- 20 The same effect is observed for conversion of butanes to aromatic hydrocarbon, but with less sensitivity to changes the process conditions of reactor **224**. Instead of operating at reactor **224** at maximum conversion of butanes to aromatic hydrocarbon X_{MB}, the specified process conditions typically result in an initial (start of run) conversion of butenes to aromatic hydrocarbon (“X_{IB}”) that is less than X_{MB}, e.g., $X_{IB} \leq 0.995 \cdot X_{MB}$, such as $\leq 0.99 \cdot X_{MB}$, or $\leq$
- 25 $0.985 \cdot X_{MB}$.

- [0102]** Dehydrocyclization conditions in reactor **334** generally include a temperature T₂ in the range of from 450 °C to 700 °C, and a pressure $P_2 \leq 35$ psia (241.3 kPa). Typically, $T_1 \leq 0.9 \cdot T_2$, e.g., $T_1 \leq 0.85 \cdot T_2$, such as $T_1 \leq 0.8 \cdot T_2$. The pressure in reactor **334** is typically less than the pressure in reactor **224**, e.g., $P_2 \leq 0.95 \cdot P_1$, such as $P_2 \leq 0.90 \cdot P_1$, or $P_2 \leq 0.85 \cdot P_1$, or
- 30 $P_2 \leq 0.8 \cdot P_1$. Typically, reaction conditions in reactor **334** include T₂ in the range of from 500 °C to 675 °C and $P_2 \leq 34$ psia (234.4 kPa), e.g., ≤ 32 psia (220.6 kPa), such as ≤ 30 psia (207 kPa), or in the range of from 10 psia (68.9 kPa) to 35 psia (241.3 kPa) or from 12 psia (82.8 kPa) to 34 psia (234.4 kPa). Generally, the reaction in reactor **334** is carried out at a C₂₊ hydrocarbon

WHSV of the specified first product with respect to the second catalyst in the range of from 0.1 hr⁻¹ to 20 hr⁻¹, e.g. 0.2 hr⁻¹ to 5 hr⁻¹, or 0.3 hr⁻¹ to 1 hr⁻¹. In congruence with the WHSV of reactor **224**, the WHSV of reactor **334** is based on C₂₊ hydrocarbon content, and is the hourly rate of C₂₊ hydrocarbon (in grams) introduced into reactor **334** per gram of second catalyst.

- 5 Those skilled in the art will appreciate that T₁ and T₂ represent average temperatures across a reaction zone, or more particularly, across a catalyst bed located within a reaction zone. Average temperature is calculated by adding the zone's inlet temperature to the zone's outlet temperature, and then dividing the sum by 2. P₁ and P₂ are not average pressures. Instead, they correspond to the inlet pressure at the specified reactor, e.g., reactor **224** for P₁ and reactor
- 10 **334** for P₂. Unlike reactor **224**, it has been found that increased reaction pressure in reactor **334** (i) decreases the yield of aromatic hydrocarbon and (ii) increases the rate of catalyst coke accumulation. A pressure of P₂ ≤ 35 psia (241.3 kPa) is generally needed to achieve a reactor **334** cycle time ≥ 50 hours.

- [0103] Contrary to expectations, it is detrimental to operate reactor **334** at a temperature
- 15 sufficient for maximum conversion of ethane, typically T₂ > 700 °C. Doing so is observed to result in a decrease in selectivity to the desired aromatic hydrocarbon product. Typically, the average temperature across any reaction zone within reactor **334** (and across any catalyst bed located within a reaction zone reactor **334**) is ≤ 700 °C. Typically, the aromatization feed is not exposed to a temperature ≥ 700 °C at the inlet of reactor **334**.

- 20 [0104] It also has been found that operating reactor **334** at a temperature > 700 °C can lead to a chemical conversion of the catalyst's dehydrogenation component and a loss of catalytic dehydrocyclization activity, particularly when the dehydrogenation component includes one or more oxide of Zn. While not wishing to be bound by any theory or model, it is believed that utilizing a temperature > 700 °C results in a conversion from the oxide form to a metallic form
- 25 of Zn, which has a greater vapor pressure than does the oxide form. The loss of catalytic dehydrocyclization activity is thus attributed at least partially to the evaporation of Zn from the catalyst. Typically, total ethane conversion in the second stage is ≤ 60%, e.g., ≤ 50, such as ≤ 40%, or in the range of from 25% to 60%, or 30% to 55%, or 30% to 50%, or 30% to 40%.

- [0105] At least to lessen the rate of catalyst coke accumulation, typically the
- 30 dehydrocyclization conditions of reactor **224** are selected to convert (i) ≥ 50 wt. %, e.g., ≥ 75 wt. %, such as ≥ 90 wt. % of the aromatization feed's C₃₊ non-aromatic hydrocarbon, but (ii) ≤ 50 wt. %, e.g., ≤ 25%, such as ≤ 10 %, or ≤ 1% of the aromatization feed's C₂ hydrocarbon. Since the feed to reactor **334** typically contains fewer C₃₊ non-aromatic hydrocarbon

compounds than does the aromatization feed, reactor **334** is typically operated under more severe conditions in order to achieve at least some ethane conversion to aromatic hydrocarbon. Those skilled in the art will appreciate that within the ranges of process parameters specified for reactor **334**, there are process conditions which if used would result in a maximum ethane conversion to aromatic hydrocarbon " X_{ME} ". Unlike conventional multi-stage processes, reactor **334** typically is not operated at X_{ME} . Instead, process conditions are generally selected so that the initial (start of run) conversion of ethane to aromatic hydrocarbon in reactor **334** " X_{2E} " is less than X_{ME} , e.g., $\leq 0.9 \cdot X_{ME}$. Typically, $X_{2E} \leq 0.85 \cdot X_{ME}$, e.g., $\leq 0.8 \cdot X_{ME}$, or $\leq 0.75 \cdot X_{ME}$. It has been found that operating stage two under conditions which provide $X_{2E} \geq X_{ME}$ lead to excessive catalyst coking, which typically necessitates a shortened cycle time in fixed bed operation. Since there is a net conversion of ethane in reactor **334**, X_{2E} is greater than zero. Since ethane can be (and typically is) produced in reactor **224**, the amount of ethane conversion in reactor **224** (X_{1E}) can be less than zero. Generally, when operating under the specified conditions using the specified feeds, X_{2E} is greater than X_{1E} . Typically, $[1 - (X_{1E} / X_{2E})]$ is ≤ 5 , e.g., ≤ 2 , such as ≤ 1 , or in the range of 0.5 to 5, or 0.6 to 2, or 0.6 to 1.

[0106] In particular aspects, the first stage reactor **224** contains at least two fixed beds of the first catalyst and the second stage reactor **334** contains at least two fixed beds of the second catalyst. Particularly in these aspects, the aromatization feed reacts in the presence of the first catalyst in reactor **224** while exposed to a temperature T_1 in the range of from 450 °C to 605 °C and a pressure P_1 in the range of from 37 psia (255.1 kPa) to 100 psia (689.5 kPa), at a space velocity (WHSV) in the range of from 0.1 hr⁻¹ to 20 hr⁻¹, such as from 0.25 hr⁻¹ to 2 hr⁻¹. That portion of the first reaction effluent which reacts in second stage reactor **334** is exposed to a temperature T_2 in the range of from 500 °C to 675 °C and a pressure $P_2 \leq 32$ psia (220.6 kPa), at a space velocity (WHSV) in the range of from 0.1 hr⁻¹ to 20 hr⁻¹, such as from 0.25 hr⁻¹ to 2 hr⁻¹, and typically less than the WHSV used when reacting the aromatization feed in reactor **224**. More particularly, $T_1 \leq 0.9 \cdot T_2$ and $P_2 \leq 0.9 \cdot P_1$, with P_2 in the range of 1 psia to 32 psia (220.6 kPa), e.g., 5 psia (34.5 kPa) to 30 psia (206.8 kPa), or 5 psia (34.5 kPa) to 29 psia (199.9 kPa).

[0107] The first and second catalysts can be selected from among any of the dehydrocyclization catalysts described in connection aspects illustrated in the single-stage aromatizer of Fig. 2. In particular aspects, the first catalyst comprises a molecular sieve component, a dehydrogenation component, and optionally a matrix component. The molecular sieve component includes ≥ 90 wt. % of an aluminosilicate in hydrogen form, the

aluminosilicate having a constraint index in the range of from 2-12 (e.g., phosphorous-modified H-ZSM-5) and a silica to alumina ratio in the range of from 50 to 80. The molecular sieve component can includes ≥ 95 wt. % of self-bound, small crystal H-ZSM-5. The dehydrogenation component includes ≥ 90 wt. % of at least one oxide of Ga. The matrix
5 component includes ≥ 75 wt. % of alumina, silica, and combinations thereof. The catalyst optionally includes ≥ 1 wt. % phosphorus, e.g., in the form of phosphorous-modified H-ZSM-5 and/or by including phosphorous in the matrix component.

[0108] In particular aspects, the second catalyst includes a molecular sieve component, a dehydrogenation component, and optionally a matrix component. The second catalyst can be
10 selected from among the same catalysts specified for use in stage 1 (the first catalyst), although typically the second catalyst has a greater acidity than does the first catalyst. For example, the molecular sieve component includes ≥ 90 wt. % of an aluminosilicate in hydrogen form, the aluminosilicate having a constraint index in the range of from 2-12 (e.g., small crystal, H-ZSM-5). Typically, (i) the second catalyst has a silica : alumina ratio in the range of from 3 to 60,
15 e.g., from 10 to 40, such as from 15 to 35, and (ii) the catalyst includes < 0.01 wt. % phosphorus.

[0109] In these aspects, the second catalyst's dehydrogenation component can include ≥ 90 wt. % of at least one oxide of Zn. The matrix component when used includes ≥ 90 wt. % of alumina, silica, and combinations thereof. The second catalyst typically includes < 0.01 wt. % phosphorus.

[0110] A second reaction effluent is produced by reacting that portion of the first reaction effluent entering reactor 334 with the specified second catalyst under the specified conditions. The second reaction effluent is conducted away as a second reaction effluent via conduit 325. Generally, the second reaction effluent includes (i) ≥ 0.5 wt. % of additional aromatic hydrocarbon, (ii) additional molecular hydrogen, and optionally methane and ethane. The
25 second reaction effluent generally includes ≥ 1 wt. % of total aromatic hydrocarbon, e.g., the total of (i) the additional aromatics and (ii) any portion of the reaction effluent's aromatics which are conveyed to the second stage but are not converted. Typically, the second reaction effluent has a total aromatic hydrocarbon content of ≥ 5 wt. %, based on the weight of the second reaction effluent, such as ≥ 10 wt. %, or in the range of from 1 wt. % to 95 wt. %, or 10
30 wt. % to 75 wt. %. The second reaction effluent's additional aromatic hydrocarbon content is typically ≥ 1 wt. %, e.g., ≥ 2 wt. %, such as ≥ 10 wt. %, or ≥ 25 wt. %, or ≥ 50 wt. %, or ≥ 75 wt. %. The process produces a desirable BTX product. Even though T_2 is greater than T_1 , it has been found that the second reaction effluent has an unexpected increase in desirable xylene

isomers, and an unexpected decrease yield of less desirable C₁₁₊ aromatic hydrocarbon.

[0111] Light hydrocarbon, e.g., ethane, can be present in the second reaction effluent. Methane, when present in the aromatization feed, does not typically convert to other hydrocarbon compounds under the conditions specified for stage 1 and/or stage 2; consequently when inter-stage methane separation is not used, substantially all of the feed methane typically is present in the second reaction effluent. The second reaction effluent typically includes additional methane, namely that produced in stage 2, e.g., by hydrogenolysis of C₂₊ hydrocarbon, and optionally that produced in stage 1 when inter-stage methane separation is decreased or not used.

10 ***Product Recovery from Second Stage Reaction Effluent***

[0112] Although the second stage reaction effluent can be recovered in separation stage 129 of recoverer 128, it is typical to utilize a second separation stage, e.g., stage 329, as shown in Fig. 3. Second separation stage 329 can be configured to operate substantially the same way, and can use substantially the same components, as separation stage 129. For example, second separation stage 329 can separate from the second reaction effluent (i) a tail gas, which is conducted away via conduit 130B, and (ii) a second product, which is conducted away via conduit 338. The second product typically comprises ≥ 50 wt. % of the second reaction effluent's aromatic hydrocarbon, e.g., ≥ 75 wt. %, or ≥ 90 wt. %. The recovery of the second product from the second reaction effluent's aromatic hydrocarbon is typically carried out at a recovery rate in the range of from 200 BPD (3.2 M³PD) to 10,000 BPD (160 M³PD), e.g., 500 BPD (7.9 M³PD) to 5000 BPD (79 M³PD), such as 1000 BPD (16 M³PD) to 4000 BPD (64 M³PD). Optionally, the second product is combined with the first product, as shown in Fig. 3. The separated tail gas of conduit 130B typically comprises molecular hydrogen, methane, and unreacted ethane.

25 ***Regeneration of the Dehydrocyclization Catalyst***

[0113] In certain aspects, the aromatizer (including, e.g., the first stage and/or second stage; and/or additional stages if used) can include one or more additional reaction zones, e.g., additional reactors (not shown). These additional reactors can be substantially the same as the others, namely of substantially the same bed configuration and contain substantially the same amount of substantially the same catalyst. Typically, the reactors of a stage operate in reaction (dehydrocyclization) mode while the additional reactors are operated in regeneration mode, and *vice versa*. Continuous or semi-continuous operation can be carried out in each stage, e.g.,

by alternating reactors and additional reactors in sequence in reaction and regeneration modes. In the aspects illustrated in Fig. 3, the first and second stages are each typically operated in dehydrocyclization mode for an average cycle time ≥ 50 hours, e.g., ≥ 75 hours, such as ≥ 100 hours, or ≥ 120 hours, at an aromatics yield that is $\geq 95\%$ of that attained at the start of
5 dehydrocyclization mode, e.g., $\geq 90\%$, such as $\geq 75\%$.

[0114] Typically, a stage's dehydrocyclization catalyst is regenerated at a temperature ≤ 700 °C. Exceeding this temperature during regeneration has been found to result in catalyst de-alumination and/or loss of structure, leading to an undesirable loss of catalyst acidity. Catalyst regeneration for any of the specified catalysts is typically carried out using procedures
10 which limit the maximum temperature to which the catalyst is exposed during regeneration to about 750 °C, more typically to about 650 °C. Conventional catalyst regeneration methods can be used, e.g., exposing the catalyst to an oxidant such as air or oxygen in air for a time sufficient to remove at least a portion of the catalyst coke, but the invention is not limited thereto. When dehydrocyclization stages 1 and/or 2 are carried out in a set of fixed-bed, adiabatic reactors in
15 series, a suitable regeneration procedure includes circulating a stream of regeneration gas containing a limited amount of oxygen, which limits the size of the exotherm where coke is burned off the catalyst. Typically, at the location where the regeneration gas enters the first (most upstream, with respect to the flow of regeneration gas) reactor, e.g., at the reactor's inlet, the regeneration gas is exposed to a temperature ≤ 350 °C, e.g., ≤ 325 °C, such as ≤ 300 °C. If
20 needed, the oxidant content of the regenerating gas can be decreased to lessen the risk of exceeding the maximum temperature.

Power Generator

[0115] Certain forms of power generator will now be described in more detail with reference to Fig. 3, which utilize as a feed the tail gas provided via conduit **130B**. The invention
25 is not limited to these forms, and this description is not meant to foreclose other forms, such as those which use a feed which comprises tail gas conveyed via conduit **130A**.

[0116] As shown in Fig. 3, tail gas is compressed in compressor **160** and then is conducted to a combustion stage of gas turbine **161**, which also includes a compression stage, and an expansion stage. The expansion and compression stages are connected via rotatable shaft **166**.
30 Oxidant of conduit **162**, e.g., oxygen, air, or oxygen in air, is compressed in the compression stage upstream of the combustion stage. Combustion produces high pressure exhaust gases, which are passed through the expansion stage, creating mechanical power (shaft power) that turns the shaft **166**. Shaft **166** is rotatably connected to electric generator **164**, which produces

electricity **165**. The lower pressure flue gas **163** still retains a significant amount of heat energy. Accordingly, a heater **230** may include one or more HRUs. Optionally, these aspects include combusting a portion of tail gas (e.g., in conduits **130A** and/or **130B**) in heater **230**.

5 **[0117]** The resulting electrical power may be used at the site or exported to an electrical grid. The amount of power produced may depend on the aromatization feed's volumetric flow rate. In examples in which the aromatization feed has a volumetric flow rate of about 50 MSCFD ($1.4 \cdot 10^6 \text{ NM}^3\text{D}$), the electrical power generated may be about 150 megawatts (MW).

10 **[0118]** While the present techniques may be susceptible to various modifications and alternative forms, the examples discussed above have been shown only by way of example. However, it should again be understood that the techniques is not intended to be limited to the particular examples disclosed herein. Indeed, the present techniques include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

CLAIMS

What is claimed is:

1. A system for producing aromatic hydrocarbon, comprising:
 - (a) a an aromatizer configured for (i) receiving a preselected amount ≥ 1 million
5 standard cubic feet per day [MSCFD] (29,000 NM³D) of an aromatization feed, the
aromatization feed comprising C₂ hydrocarbon and C₃₊ non-aromatic hydrocarbon and having
a preselected C₂₊ non-aromatic hydrocarbon concentration in the range of from 15 mole % to
90 mole % per mole of aromatization feed, and (ii) aromatization of (A) at least a portion of
the aromatization feed's C₃₊ non-aromatic hydrocarbon and (B) at least a portion of the
10 aromatization feed's C₂ hydrocarbon to produce a reaction effluent comprising molecular
hydrogen, non-aromatic hydrocarbon, and aromatic hydrocarbon; and
 - (b) a product recoverer in fluidic communication with the aromatizer, the product
recoverer being configured for recovering at least first and second products from the reaction
effluent, wherein the first product comprises at least a portion of the reaction effluent's
15 aromatic hydrocarbon and the second product comprises a tail gas containing (i) at least a
portion of the reaction effluent's molecular hydrogen and (ii) at least a portion of the reaction
effluent's non-aromatic hydrocarbon.
2. The system of claim 1, wherein the system further comprises a feed pretreater
configured for (A) receiving ≥ 2 MSCFD (57,000 NM³D) of a gaseous feed and (B) producing
20 the aromatization feed from the gaseous feed, the gaseous feed comprising 0 mole % to 98
mole % methane, 1 mole % to 50 mole % of C₂ hydrocarbon and 1 mole % to 40 mole % of
C₃₊ non-aromatic hydrocarbon.
3. The system of claim 2, wherein the feed pretreater includes:
 - (i) at least one heat transfer stage having (A) an inlet in fluidic communication with
25 the feed conduit, and (B) an outlet, the heat transfer stage being configured for the transfer of
heat away from the gaseous feed in order to condense a portion of the gaseous feed at a
predetermined dew point, and
 - (ii) at least one vapor-liquid separator, the vapor-liquid separator having an inlet in
fluidic communication with the heat transfer stage, at least one separator drum and first and
30 second outlets, wherein:
 - (A) the separator's inlet is configured for receiving the feed's gaseous and

condensed portions from the heat transfer stage,

(B) the separator drum is configured for disengaging the feed's gaseous and condensed portions to produce a bottoms stream comprising the aromatization feed and an overhead stream comprising separated gaseous hydrocarbon,

5 (C) the separator's first outlet is configured for conveying the separated gaseous portion away from the pretreater, and

(D) the separator's second outlet is configured for conveying the preselected amount of the aromatization feed to the aromatizer.

4. The system of any of claims 1-3, wherein the system further comprises a tail gas
10 converter in fluidic communication with the product recoverer, the tail gas converter including at least one molecular hydrogen separation stage and at least one power generation stage, wherein:

(i) the molecular hydrogen separation stage includes an inlet for receiving the tail gas from the product recovered and first and second outlets,

15 (ii) a hydrogen separator in fluidic communication with the molecular hydrogen separation stage, the hydrogen separator being configured for separating from the tail gas hydrogen-rich stream comprising ≥ 75 wt. % of the tail gas's molecular hydrogen and a hydrogen lean stream comprising ≥ 25 wt. % of the tail gas's non-aromatic hydrocarbon,

(iii) the molecular hydrogen separation stage's first outlet is configured for
20 transferring to the power generation stage at least a portion of the hydrogen-rich stream's molecular hydrogen,

(iv) power generation stage includes at least one fired heater and/or at least one gas turbine having a rotatable shaft connected to at least one electric generator,

(v) the gas turbine is configured for combusting at least a portion of the hydrogen-
25 rich stream to produce shaft power;

(vi) the electric generator is configured to convert at least a portion of the shaft power to electricity, at least a portion of the electricity being utilized for supplying heat to the aromatizer,

(vii) the fired heater is configured for combusting at least a portion of the hydrogen-
30 rich stream to produce heat, at least a portion of the heat being supplied to the aromatizer; and

(viii) the molecular hydrogen separation stage's second outlet is configured for conveying raffinate away from the tail gas converter.

5. The system of any of claims 1-4, wherein:

(i) the aromatizer includes at least one inlet, at least one reactor, and at least one
5 outlet,

(ii) the aromatizer's inlet is configured for receiving the aromatization feed and conveying the aromatization feed to the reactor,

(iii) the reactor is configured to contact the aromatization feed with at least one bed of a dehydrocyclization catalyst at a temperature range of from 400 °C to 650 °C, a pressure in
10 the range of from 100 kPa to 2200 kPa, and a space velocity in the range of 0.1 hr⁻¹ to 20 hr⁻¹ to produce the aromatizer effluent, and

(iv) the aromatizer's outlet is configured to transfer at least a portion of the reaction effluent to the product recoverer.

6. The system of any of claims 2-5, wherein the pretreater receives 10 MSCFD (290,000
15 NM³D) to 150 MSCFD (4.3•10⁶ NM³D) of the gaseous feed, the preselected amount of aromatization feed is in the range of from 2 MSCFD (57,000 NM³D) to 80 MSCFD (2.3•10⁶ NM³D), and the product recoverer recovers ≥ 90 wt. % of the reaction effluent's aromatic hydrocarbon at a recovery rate in the range of from 200 BPD (3.2 M³PD) to 10000 BPD (160 M³PD).

20 7. The system of any of claims 2-6, wherein the gaseous feed includes an associated gas comprising 0 mole % to 95 mole % of methane, 5 mole % to 50 mole % of ethane, 2 mole % to 40 mole % of propane, 0.1 mole % to 30 mole % of i-butane, 1 mole % to 30 mole % of n-butane, and 0.05 mole % to 25 mole % of i-pentane.

8. The system of any of claims 2-7, wherein at least one of the pretreater, the aromatizer,
25 and the recoverer is in a form of one or more mobile modules.

9. The system of claim 3, wherein:

(i) the pretreater's first heat transfer stage includes at least one heat exchanger in indirect thermal contact with a flow of refrigerant,

(ii) the first heat exchanger is adapted to indirectly transfer first, second, and third
30 portions of the heat transferred from the gaseous feed, the first portion being transferred to the refrigerant, the second portion being transferred to the separated gaseous hydrocarbon, and the

third portion being transferred to the aromatization feed, and

- (iii) the second heat transfer stage is configured for removing an amount of heat from the flow of refrigerant, with the amount of heat varying by no more than $\pm 50\%$ when the condensed portion that is condensed from the gaseous feed has a volume variation of $\leq \pm 10\%$.

10. The modular system of claim 8, wherein at least one of the mobile modules is supported by one or more skids, each skid having a gross weight $\leq 100,000$ pounds (45,360 kg), a width ≤ 15 feet (4.6 m), and a height ≤ 15 feet (4.6 m).

11. A hydrocarbon conversion process, comprising:

- 10 (a) providing a preselected amount ≥ 1 million standard cubic feet per day [MSCFD] (29,000 NM³D) of an aromatization feed comprising C₂ hydrocarbon and C₃₊ non-aromatic hydrocarbon, the aromatization feed having a preselected C₂₊ non-aromatic hydrocarbon concentration in the range of from 15 mole % to 90 mole % per mole of aromatization feed;

- 15 (b) reacting the aromatization feed in the presence of at least one dehydrocyclization catalyst under catalytic dehydrocyclization conditions to produce a reaction effluent comprising (i) non-aromatic hydrocarbon and (ii) aromatic hydrocarbon and molecular hydrogen, the aromatic hydrocarbon and the molecular hydrogen being formed by dehydrocyclization of at least a portion of the aromatization feed's C₂ hydrocarbon and/or the
20 aromatization feed's C₃₊ non-aromatic hydrocarbon; and

- (c) recovering at least first and second products from the reaction effluent, wherein the first product comprises at least a portion of the reaction effluent's aromatic hydrocarbon and the second product comprises a tail gas containing (i) at least a portion of the reaction effluent's molecular hydrogen and (ii) at least a portion of the reaction effluent's non-aromatic
25 hydrocarbon.

12. The process of claim 11, further comprising producing the aromatization feed by pretreating ≥ 2 MSCFD (57,000 NM³D) of a gaseous feed, the gaseous feed comprises 0 mole % to 98 mole % methane, 1 mole % to 50 mole % of C₂ hydrocarbon and 1 mole % to 40 mole % of C₃₊ non-aromatic hydrocarbon.

- 30 13. The process of claim 12, wherein the gaseous feed includes an associated gas comprising 0 mole % to 95 mole % of methane, 5 mole % to 50 mole % of ethane, 2 mole % to 40 mole % of propane, 0.1 mole % to 30 mole % of i-butane, 1 mole % to 30 mole % of n-

butane, and 0.05 mole % to 25 mole % of i-pentane.

14. The process of claims 12 or 13, wherein the gaseous feed is provided in an amount in the range of from 10 MSCFD (290,000 NM³D) to 150 MSCFD (4.3•10⁶ NM³D), the preselected amount of aromatization feed is in the range of from 2 MSCFD (57,000 NM³D) to 80 MSCFD (2.3•10⁶ NM³D), and step (c) includes recovering ≥ 90 wt. % of the aromatization effluent's aromatic hydrocarbon at a recovery rate in the range of from 200 BPD (3.2 M³PD) to 10,000 BPD (160 M³PD).

15. The process of any of claims 12- 14, wherein the pretreating includes (i) transferring heat away from the gaseous feed in at least a first heat transfer stage in order to partially condense the gaseous feed at a predetermined dew point, and (ii) separating from the partially condensed feed an overhead stream comprising gaseous hydrocarbon and a bottoms stream, the bottoms stream being the aromatization feed.

16. The process of claim 15, wherein the partial condensation of the gaseous feed is carried out at a pressure in the range of from 300 psia (2068 kPa) to 2000 psia (13,800 kPa), with the predetermined dew point being in the range of from - 40 °F (-40 °C) to -20 °F (-28.9 °C).

17. The process of claims 15 or 16, wherein:

(i) the first heat transfer stage includes at least one heat exchanger in indirect thermal contact with a flow of refrigerant,

(ii) the heat exchanger indirectly transfers first, second, and third portions of the heat transferred from the gaseous feed, the first portion being transferred to the refrigerant, the second portion being transferred to the separated gaseous hydrocarbon, and the third portion being transferred to the aromatization feed, and

(iii) the pretreating further includes conducting the flow of refrigerant from the first heat transfer stage to a second heat transfer stage, and removing a quantity of heat from the refrigerant in the second heat transfer stage, the quantity of heat varying by no more than +/- 50% when the condensed portion that is condensed from the gaseous feed has a volume variation of $\leq \pm 10$ %.

18. The process of claim 17, further comprising:

(d) separating from the tail gas an extract comprising ≥ 75 wt. % of the tail gas's molecular hydrogen and a raffinate comprising ≥ 90 wt. % of the tail gas's non-aromatic hydrocarbon;

(e) providing at least one gas turbine connected via at least one rotatable shaft for providing shaft power to at least one electric generator;

(f) combusting at least a portion of the extract's molecular hydrogen in the gas turbine to power the shaft;

5 (g) converting at least a portion of the shaft power to electricity, at least a portion of the electricity being utilized for supplying heat to the reaction of step (b).

19. The process of claim 18, wherein the second heat transfer stage includes at least one refrigerant compressor, at least part of the refrigerant compressor's power being obtained from the gas turbine and/or the electric generator.

10 20. The process of any of claims 11-15, wherein:

(i) the reaction of step (b) is carried out in at least one first reactor,

(ii) the first reactor includes at least one bed of the dehydrocyclization catalyst, and

(iii) the catalytic dehydrocyclization conditions in the first reactor include a first temperature T_1 in the range of from 400 °C to 650 °C, a first pressure P_1 in the range of from
15 100 kPa to 2200 kPa, and a first space velocity in the range of 0.1 hr⁻¹ to 20 hr⁻¹.

21. The process of claim 20, further comprising:

(h) conducting at least a portion of the tail gas to a second reactor, the second reactor containing at least one bed of a second dehydrocyclization catalyst, and

(i) reacting the tail gas in the second reactor in the presence of the second
20 dehydrocyclization catalyst under second dehydrocyclization conditions which include a temperature T_2 in the range of from 500 °C to 675 °C, a pressure $P_2 \leq 30$ psia (207 kPa), and a weight hourly space velocity in the range of from 0.1 hr⁻¹ to 20 hr⁻¹, to produce a second reactor product containing additional aromatic hydrocarbon, additional molecular hydrogen, and additional non-aromatic hydrocarbon, wherein

25 (i) the T_1 is in the range of from 450 °C to 605 °C, P_1 is in the range of from 37 psia (255 kPa) to 80 psia (522 kPa), and

(ii) T_2 is $> T_1$ and/or $P_1 > P_2$.

22. The process of claim 21, wherein

(i) the first catalyst comprises at least 10 wt. % of a first molecular sieve component
30 and at least 0.005 wt. % of a first dehydrogenation component,

(ii) the second catalyst comprises at least 10 wt. % of a second molecular sieve component and at least 0.005 wt. % of a second dehydrogenation component;

(iii) the first and second molecular sieve components each comprise (i) one or more of MCM-22, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, and ZSM-48 and

5 (iv) the first and second dehydrogenation components each comprise one or more of Ga, Zn, Cu, Re, Mo, W, La, Fe, Ag, Pt, and Pd.

23. The process of claim 21, further comprising removing molecular hydrogen from the tail gas upstream of the second reactor.

24. The process of claim 15 wherein the overhead stream has a Wobbe Index in the range of from 49.01 MJ/sm³ to 52.22 MJ/sm³ and has a heating value in the range of from 36.07 MJ/sm³ to 41.40 MJ/sm³.

25. The process of claim 16, wherein:

15 (i) the aromatization feed comprises C₂ hydrocarbon in an amount in the range of from 10 mole % to 35 mole % and C₃₊ hydrocarbon in an amount in the range of from 40 mole % to 50 mole %, and the first product is recovered in an amount that varies by no more than +/- 25% when (A) the preselected amount of aromatization feed is in the range of from 5 MSCFD (140,000 NM³D) to 35 MSCFD (1•10⁶ NM³D), (B) the amount gaseous feed is in the range of from 30 (860,000 NM³D) MSCFD to 140 MSCFD (4•10⁶ NM³D), and (C) the gaseous feed has a molar ratio of C₂ hydrocarbon to C₃₊ non-aromatic hydrocarbon in the range of from 20 0.5 to 1.5.

26. A system for producing aromatic hydrocarbon, comprising:

(a) at least one feed conduit for conveying from a hydrocarbon source an amount $\geq$ 2 million standard cubic feet per day [MSCFD] of a gaseous feed comprising C₂ hydrocarbon and C₃₊ non-aromatic hydrocarbon;

25 (b) a feed pretreater in fluidic communication with the feed conduit, the feed pretreater being configured for producing a preselected amount $\geq$ 1 MSCFD of a pretreated feed from the gaseous feed, the pretreated feed having a preselected C₂₊ non-aromatic hydrocarbon concentration in the range of from 55 mole % to 80 mole % per mole of pretreated feed;

30 (c) an aromatizer in fluidic communication with the feed pretreater, the aromatizer being configured for aromatization of (i) at least a portion of the pretreated feed's C₃₊ non-

aromatic hydrocarbon and (ii) at least a portion of the pretreated feed's C₂ hydrocarbon to produce an reaction effluent comprising molecular hydrogen, non-aromatic hydrocarbon, and aromatic hydrocarbon; and

- 5 (d) a product recoverer in fluidic communication with the aromatizer, the product recoverer being configured for recovering at least first and second products from the reaction effluent, wherein the first product comprises at least a portion of the reaction effluent's aromatic hydrocarbon and the second product comprises a tail gas containing (i) at least a portion of the reaction effluent's molecular hydrogen and (ii) at least a portion of the reaction effluent's non-aromatic hydrocarbon.

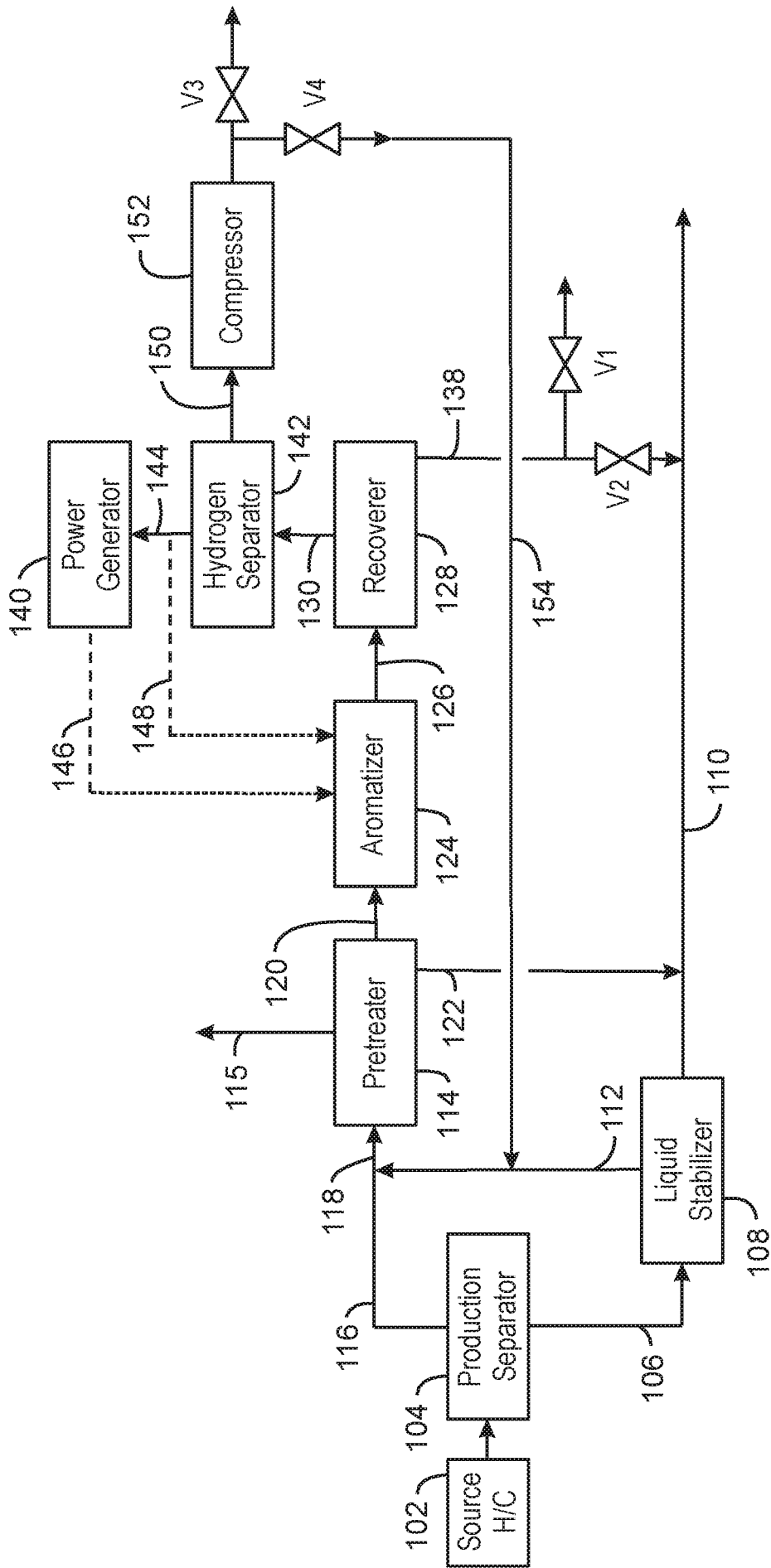
10 27. A hydrocarbon conversion process, comprising:

(a) providing a gaseous feed at a volumetric flow rate ≥ 2 million standard cubic feet per day [MSCFD] (58,000 NM³D), the gaseous feed comprising C₂ hydrocarbon and C₃₊ non-aromatic hydrocarbon;

15 (b) controlling the gaseous feed's volumetric flow rate inversely with the gaseous feed's C₂₊ hydrocarbon concentration and separating from the gaseous feed a preselected amount ≥ 1 MSCFD (29,000 NM³D) of a pretreated feed, the pretreated feed having a preselected C₂₊ non-aromatic hydrocarbon concentration in the range of from 55 mole % to 80 mole % per mole of pretreated feed;

20 (c) reacting the pretreated feed in the presence of at least one dehydrocyclization catalyst under catalytic dehydrocyclization conditions to produce a reaction effluent comprising (i) non-aromatic hydrocarbon and (ii) aromatic hydrocarbon and molecular hydrogen, the aromatic hydrocarbon and the molecular hydrogen being formed by dehydrocyclization of at least a portion of the pretreated feed's C₂ hydrocarbon and/or the pretreated feed's C₃₊ non-aromatic hydrocarbon; and

25 (d) recovering at least first and second products from the reaction effluent, wherein the first product comprises at least a portion of the reaction effluent's aromatic hydrocarbon and the second product comprises a tail gas containing (i) at least a portion of the reaction effluent's molecular hydrogen and (ii) at least a portion of the reaction effluent's non-aromatic hydrocarbon.



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FIG. 1

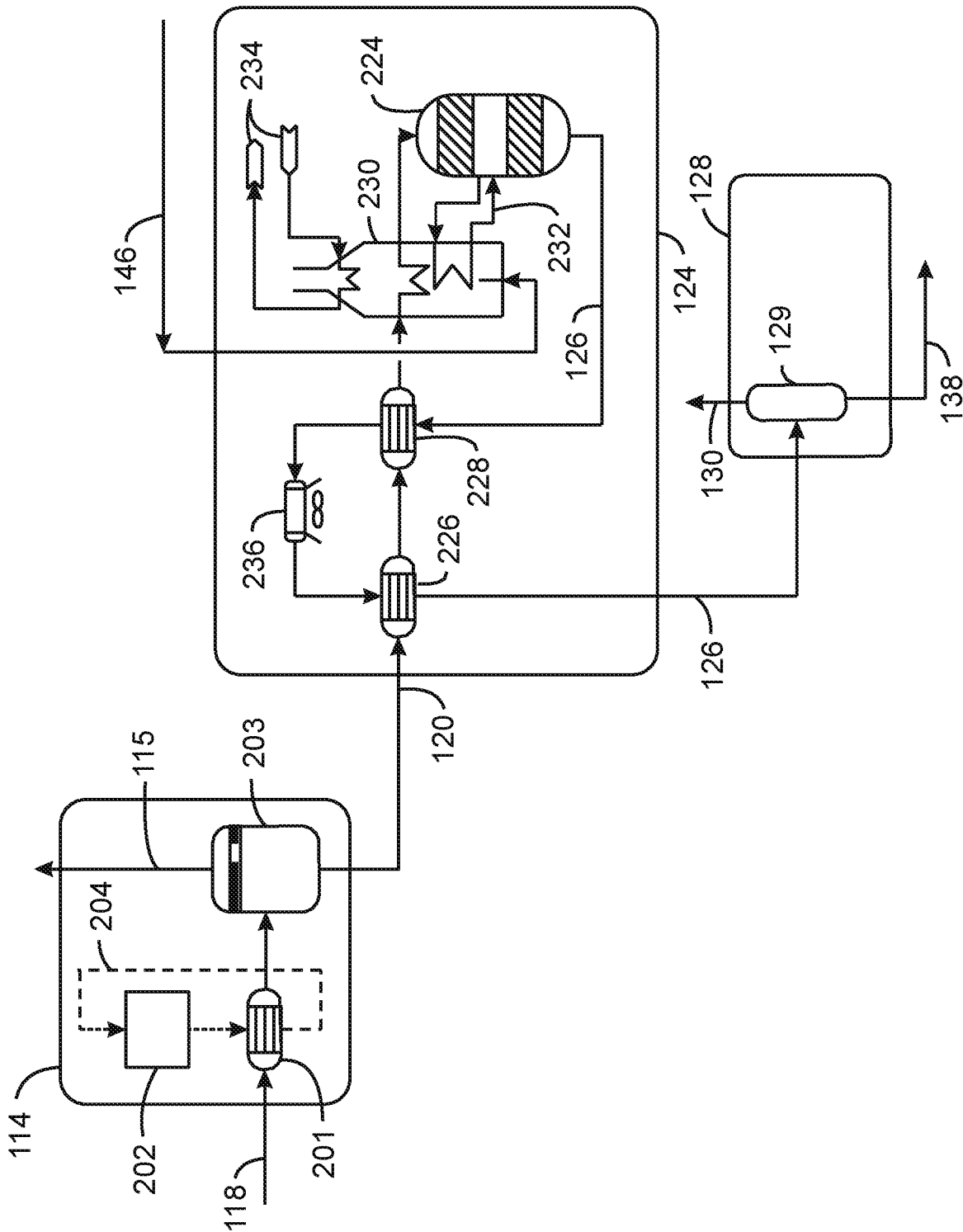


FIG. 2

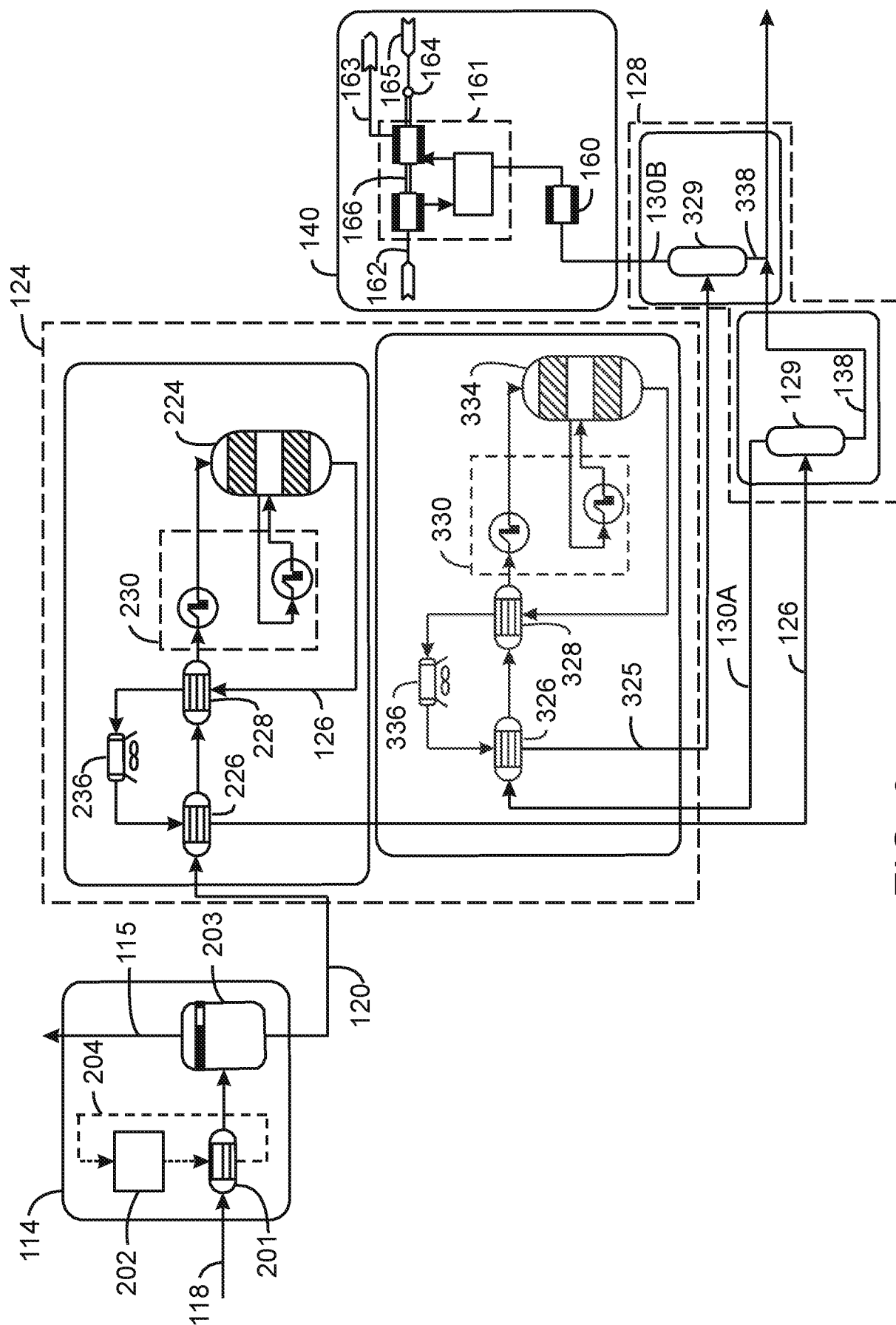


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/047530

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J29/064 C07C2/76 C07C15/02
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)
B01J C07C

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/053747 A1 (SHELL OIL CO [US]; SHELL INT RESEARCH [NL]; IYER MAHESH VENKATARAMAN []) 5 May 2011 (2011-05-05) claims; examples -----	1-27
X	WO 2009/105447 A1 (SHELL OIL CO [US]; SHELL INT RESEARCH [NL]; LAURITZEN ANN MARIE [US];) 27 August 2009 (2009-08-27) claims; examples -----	1-27

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

22 September 2016

Date of mailing of the international search report

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/047530

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011053747 A1	05-05-2011	AU 2010313369 A1 CN 102648169 A EA 201290279 A1 US 2012240467 A1 WO 2011053747 A1	10-05-2012 22-08-2012 28-12-2012 27-09-2012 05-05-2011
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