

US 20170275217A1

### (19) United States

## (12) Patent Application Publication (10) Pub. No.: US 2017/0275217 A1

Weinberger et al.

Sep. 28, 2017 (43) Pub. Date:

#### PROCESS FOR SEPARATING HYDROCARBON COMPOUNDS

Applicant: Siluria Technologies, Inc., San Francisco, CA (US)

Inventors: Sam Weinberger, San Francisco, CA (US); Justin Dwight Edwards, League City, TX (US); Julian Wolfenbarger, Landenberg, PA (US); Srinivas R. Vuddagiri, Davis, CA (US); Iraj Isaac Rahmim, San Francisco, CA (US)

Appl. No.: 15/354,886

Nov. 17, 2016 (22)Filed:

### Related U.S. Application Data

- Continuation of application No. 14/820,460, filed on (63)Aug. 6, 2015, now Pat. No. 9,527,784, which is a continuation of application No. 13/739,954, filed on Jan. 11, 2013, now Pat. No. 9,133,079.
- Provisional application No. 61/586,711, filed on Jan. 13, 2012.

#### **Publication Classification**

Int. Cl. (51)C07C 2/84 (2006.01)C10G 27/04 (2006.01)

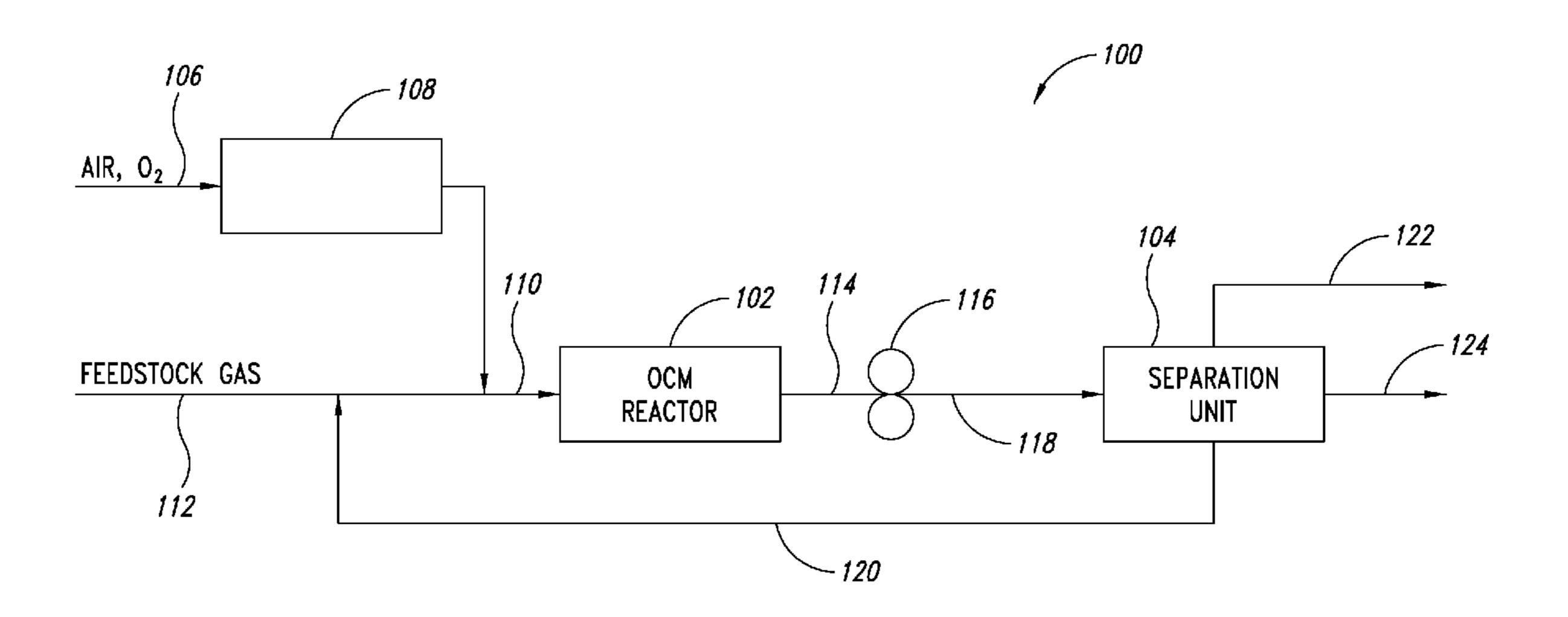
C10G 29/20	(2006.01)
C07C 9/06	(2006.01)
F25J 3/02	(2006.01)
C07C 11/04	(2006.01)
C10G 31/06	(2006.01)

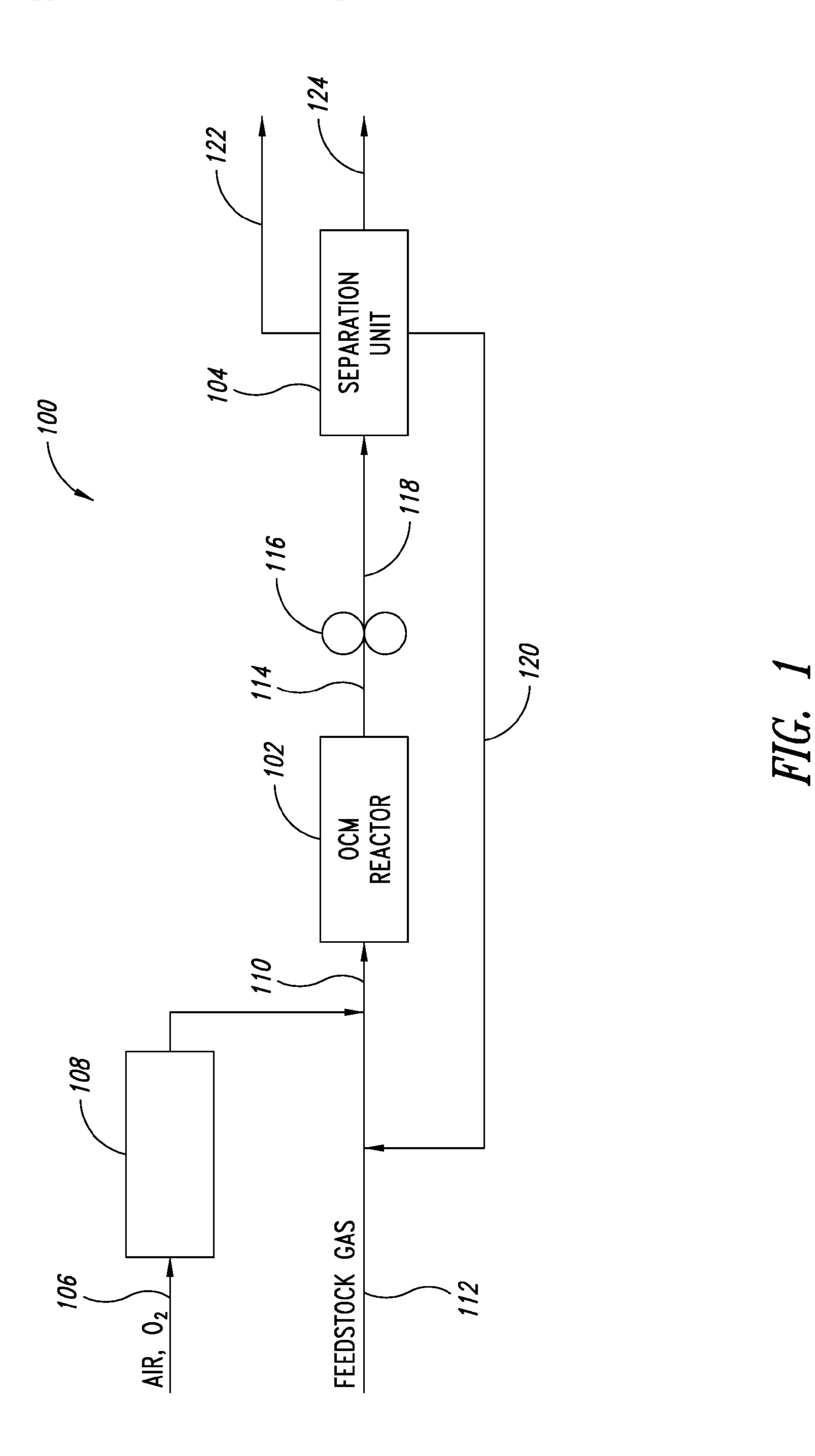
U.S. Cl. (52)CPC ...... *C07C 2/84* (2013.01); *C10G 31/06* (2013.01); F25J 2220/02 (2013.01); F25J 2235/60 (2013.01); F25J 2210/12 (2013.01); C10G 27/04 (2013.01); F25J 2240/02 (2013.01); *C10G 29/205* (2013.01); *F25J 2215/62* (2013.01); *F25J 3/0238* (2013.01); **F25J 3/0219** (2013.01); F25J 2245/02 (2013.01); *F25J 3/0242* (2013.01); *F25J 3/0233* (2013.01); *F25J 2230/30* (2013.01); **F25J 3/025**7 (2013.01); F25J 2205/04 (2013.01); *C07C* 11/04 (2013.01); *C07C* 9/06

(2013.01)

#### ABSTRACT (57)

Disclosed herein are processes for producing and separating ethane and ethylene. In some embodiments, an oxidative coupling of methane (OCM) product gas comprising ethane and ethylene is introduced to a separation unit comprising two separators. Within the separation unit, the OCM product gas is separated to provide a  $C_2$ -rich effluent, a methane-rich effluent, and a nitrogen-rich effluent. Advantageously, in some embodiments the separation is achieved with little or no external refrigeration requirement.





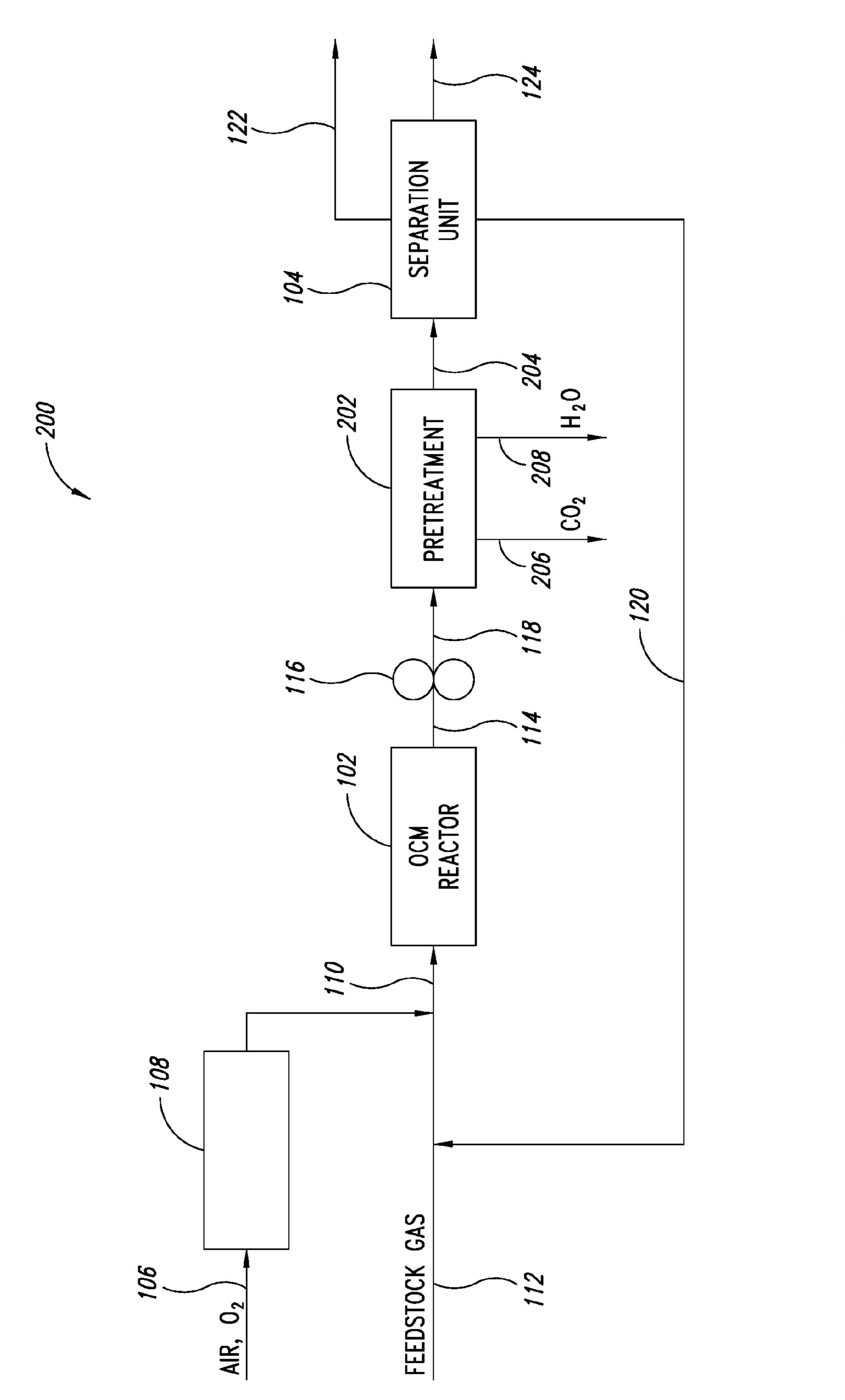
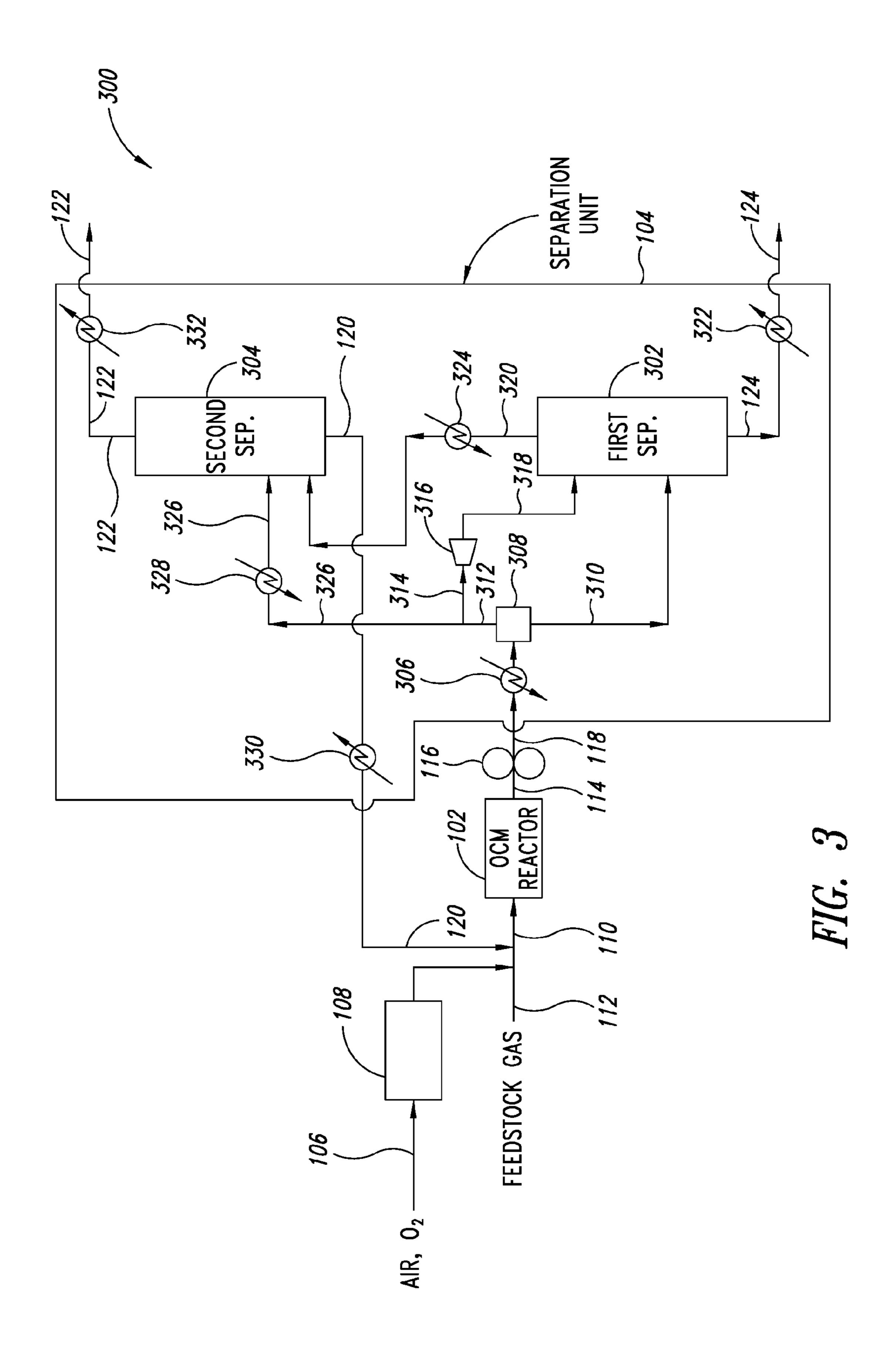
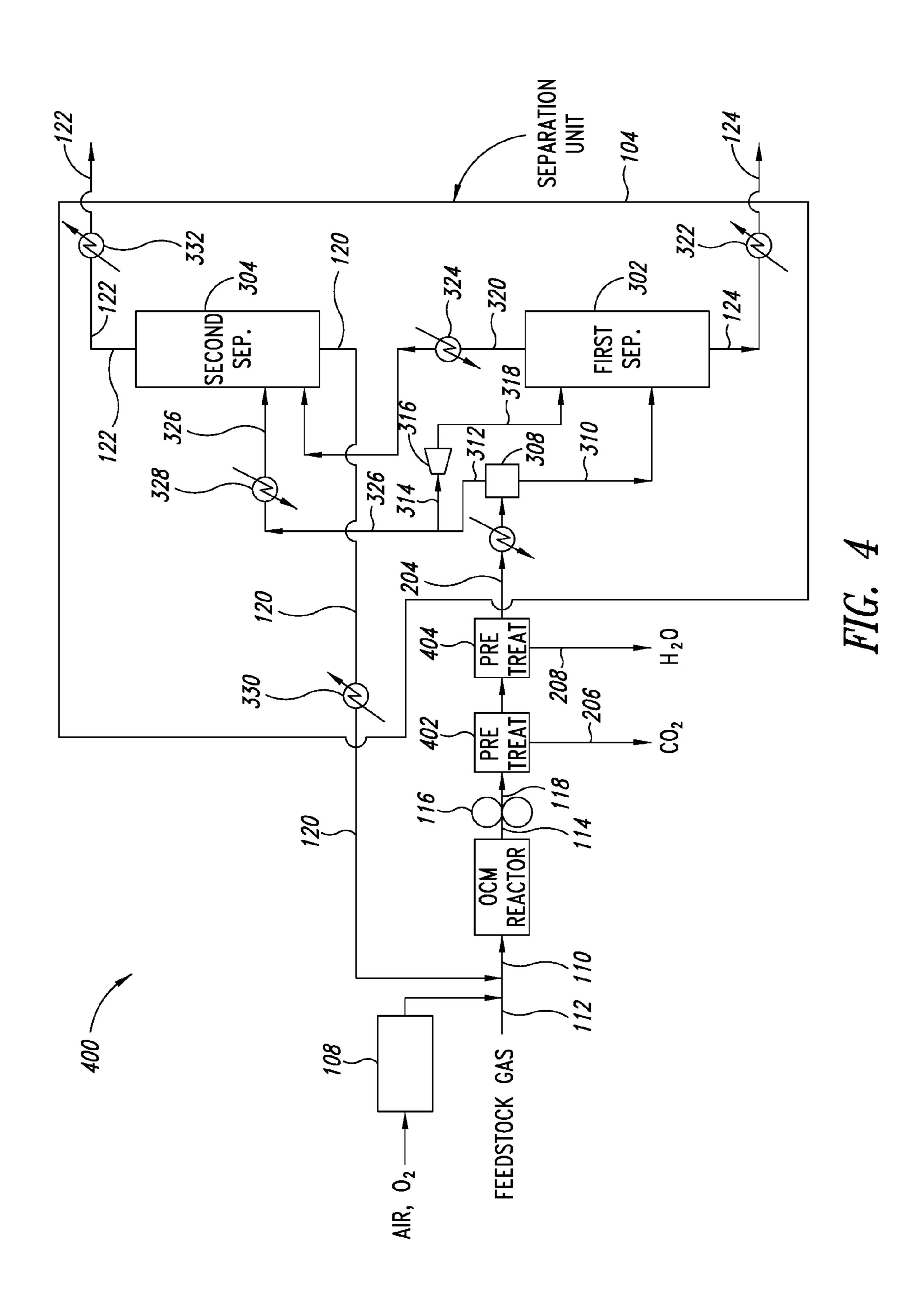
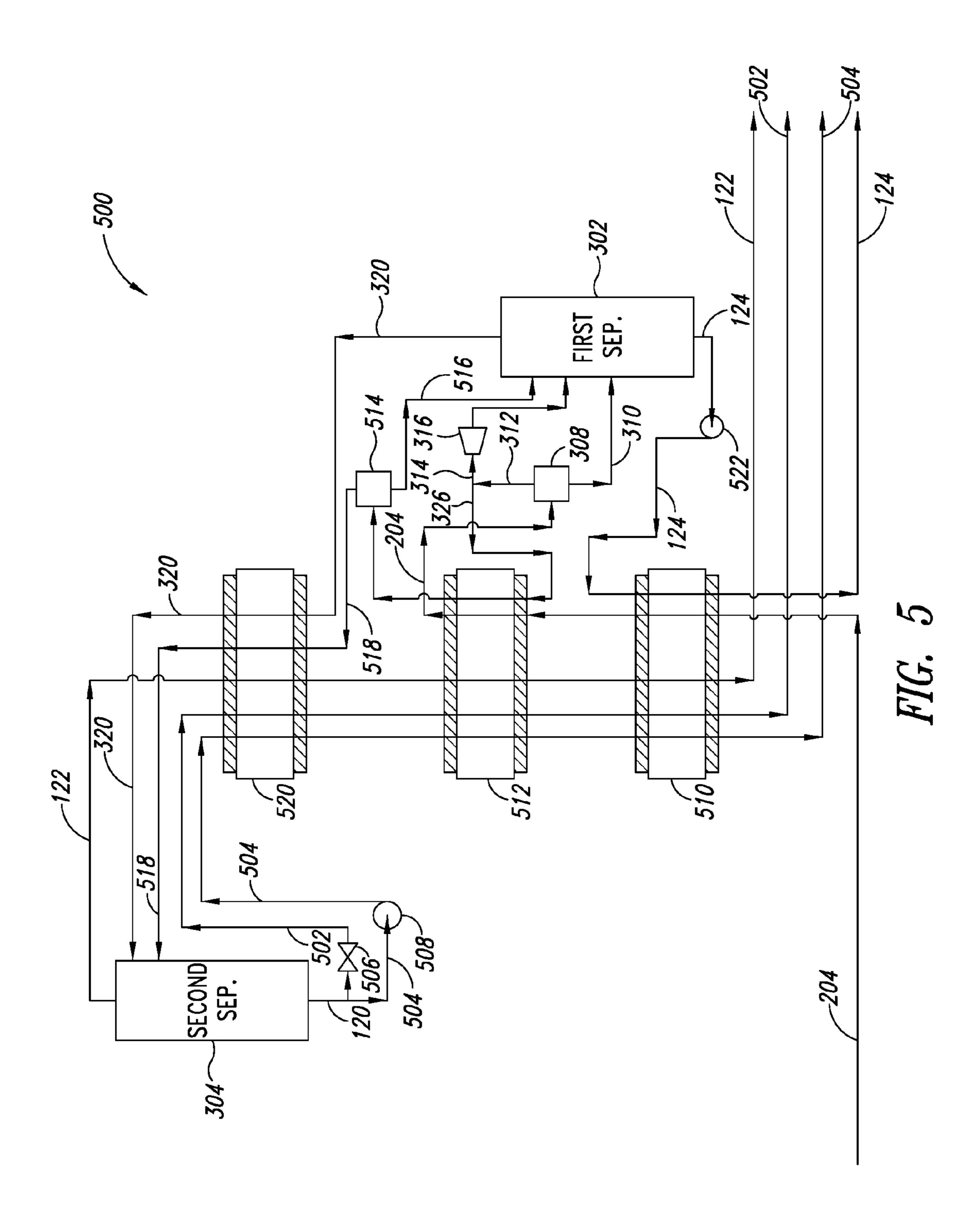


FIG. 2







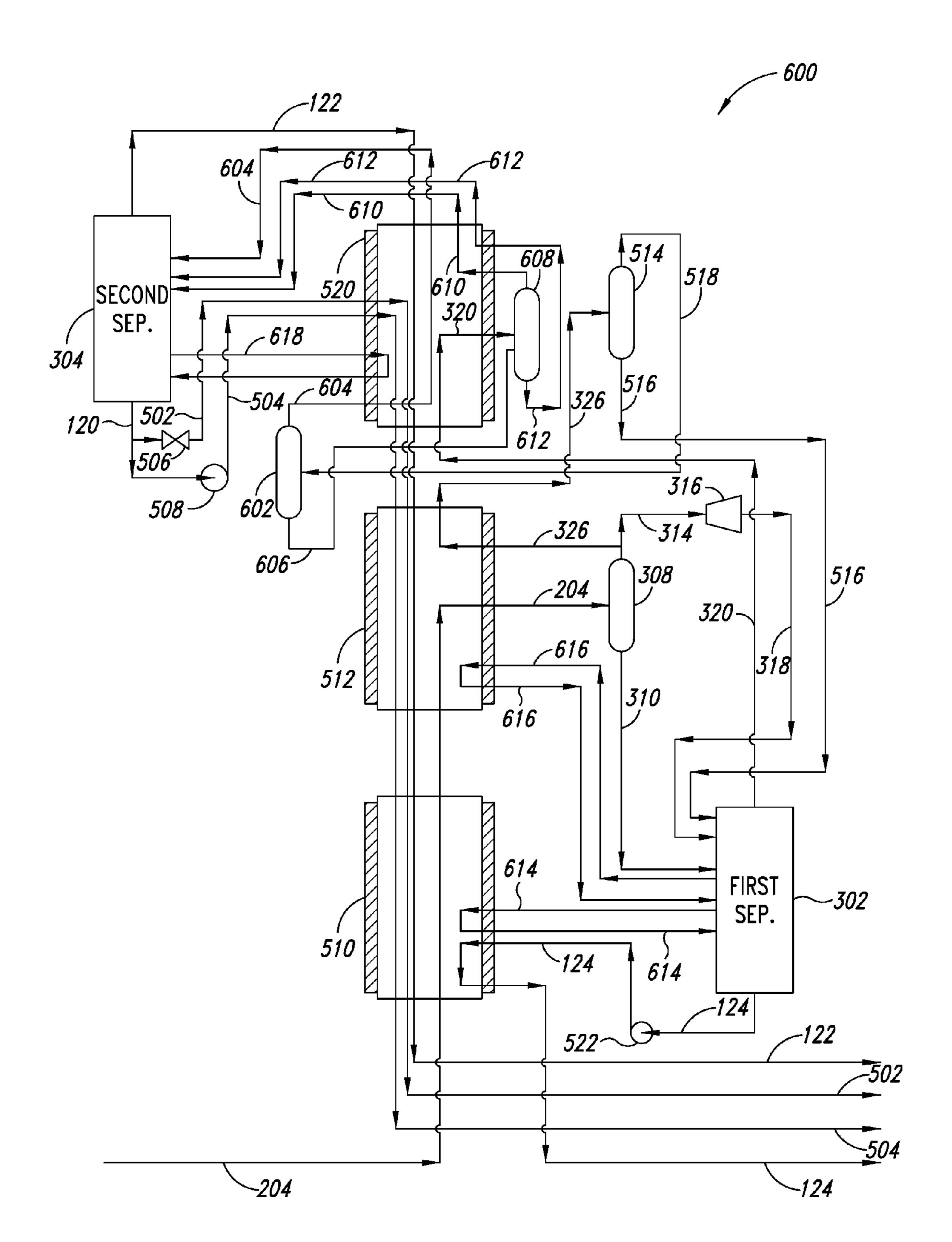
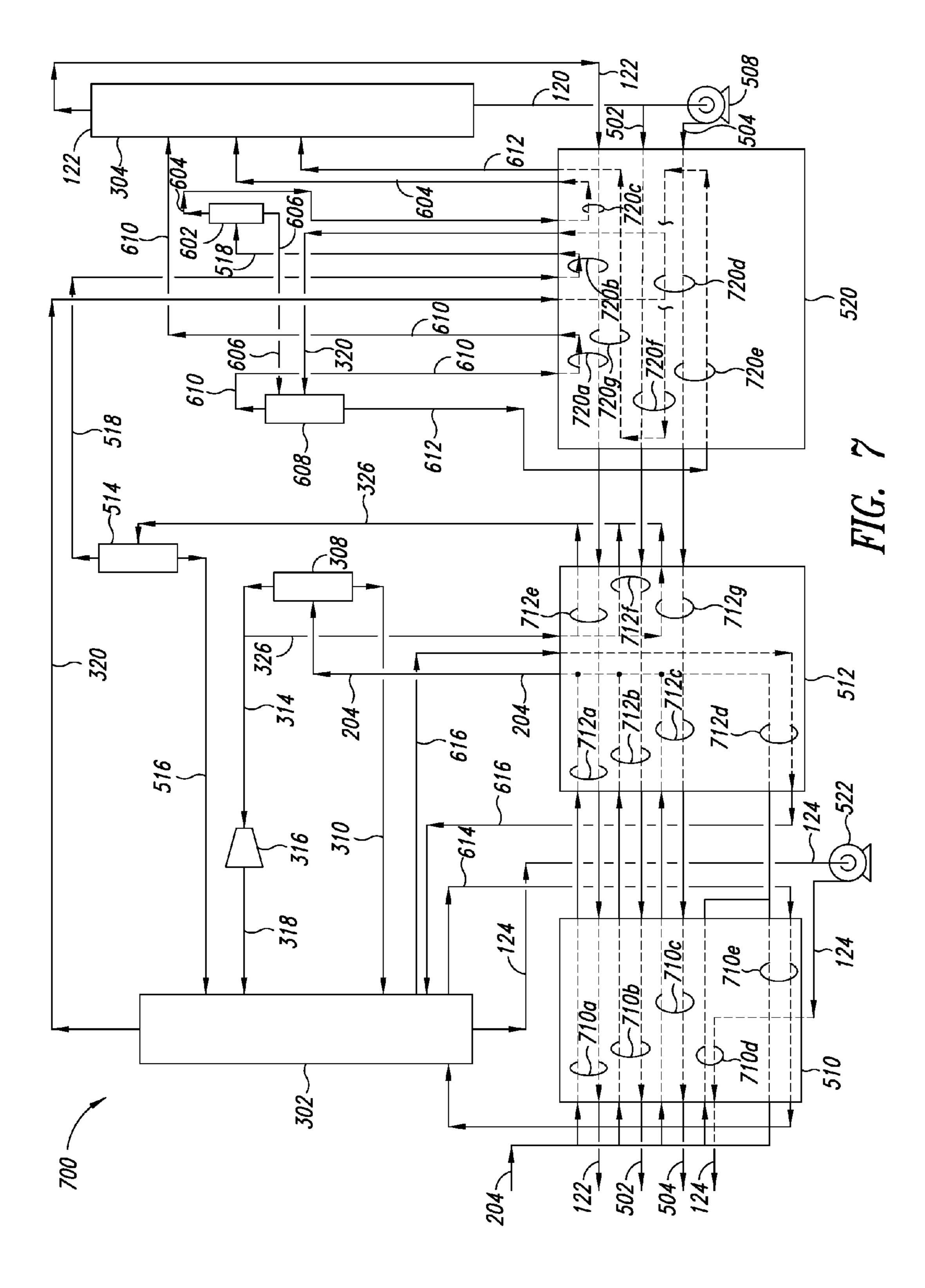


FIG. 6



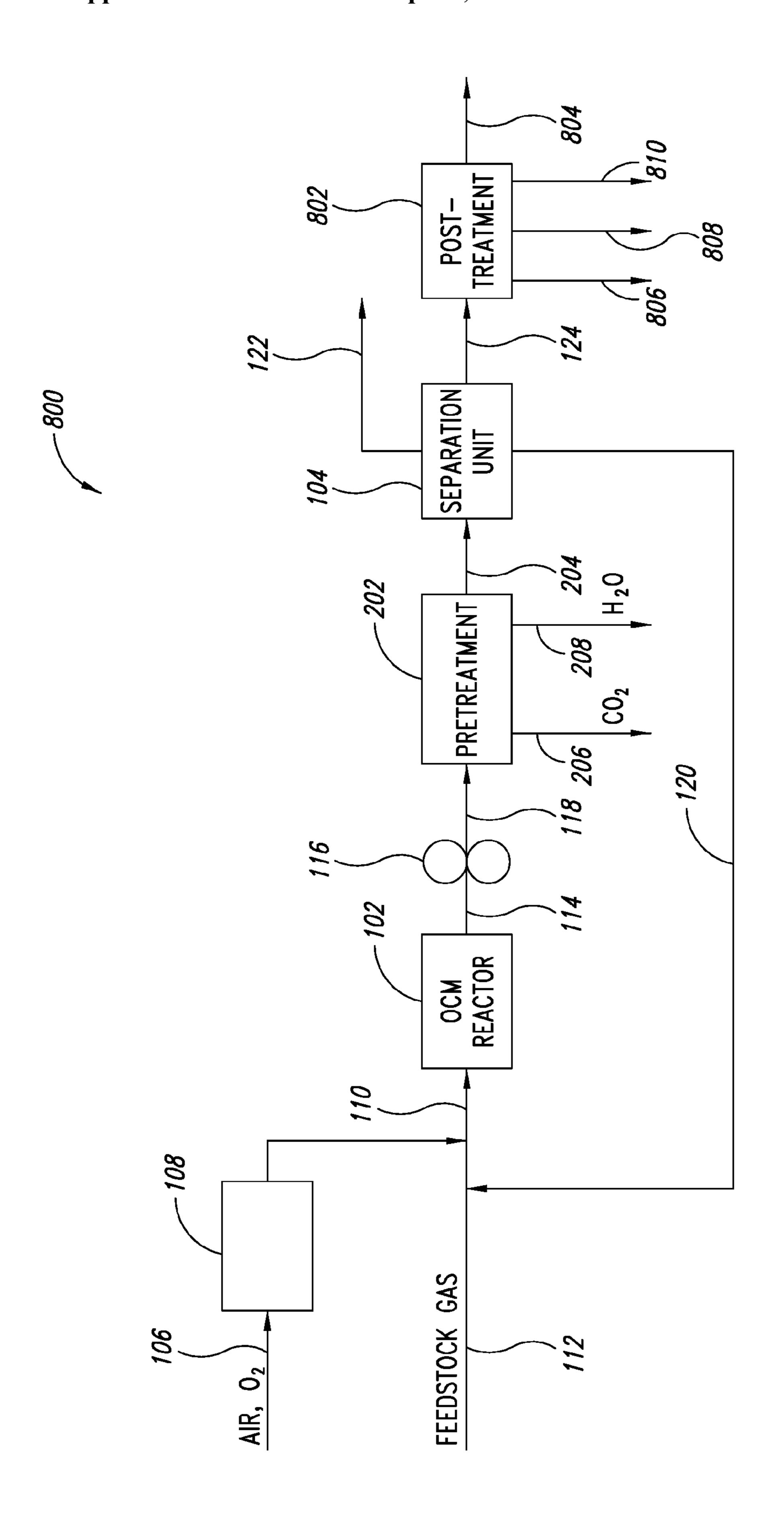


FIG. 8

#### PROCESS FOR SEPARATING HYDROCARBON COMPOUNDS

#### CROSS REFERENCE

[0001] This application is a continuation application of U.S. patent application Ser. No. 14/820,460, filed Aug. 6, 2015, which is a continuation application of U.S. patent application Ser. No. 13/739,954, filed Jan. 11, 2013, now U.S. Pat. No. 9,133,079, which claims the benefit of U.S. Provisional Patent Application Ser. No. 61/586,711, filed Jan. 13, 2012, each of which is incorporated herein by reference in its entirety.

#### BACKGROUND

[0002] Technical Field

[0003] This disclosure generally relates to selectively separating carbon compounds containing at least two carbon atoms from a mixed gas stream provided by a chemical process.

[0004] Description of the Related Art

[0005] The modern petrochemical industry makes extensive use of cracking and fractionation technology to produce and separate various desirable compounds from crude oil. Cracking and fractionation operations are energy intensive and generate considerable quantities of greenhouse gases. The gradual depletion of worldwide petroleum reserves and the commensurate increase in petroleum prices places extraordinary pressure on refiners to minimize losses and improve efficiency when producing products from existing feedstocks, and also to seek viable alternative feedstocks capable of providing affordable hydrocarbon intermediates and liquid fuels to downstream consumers.

[0006] Methane provides an attractive alternative feedstock for the production of hydrocarbon intermediates and liquid fuels due to its widespread availability and relatively low cost when compared to crude oil. Worldwide methane reserves are estimated in the hundreds of years at current consumption rates and new production stimulation technologies promise to make formerly unattractive methane deposits commercially viable.

[0007] Used in the production of polyethylene plastics, polyvinyl chloride, ethylene oxide, ethylene chloride, ethylbenzene, alpha-olefins, linear alcohols, vinyl acetate, and fuel blendstocks such as but not limited to aromatics, alkanes, alkenes, ethylene is one of the most important commodity chemical intermediates currently produced. With economic growth in developed and developing portions of the world, demand for ethylene and ethylene based derivatives continues to increase. Currently, ethylene production is limited to high volume production as a commodity chemical in a relatively large steam cracker or other petrochemical complex setting due to the high cost of the crude oil feedstock and the large number of hydrocarbon byproducts generated in the crude oil cracking process. Producing ethylene from far more abundant and significantly less expensive natural gas provides an attractive alternative to ethylene derived from crude oil. Oligomerization processes can be used to further convert ethylene into longer chain hydrocarbons such as C<sub>6</sub> and C<sub>8</sub> hydrocarbons useful for polymer gasoline and high value specialty chemicals.

[0008] The conversion of methane to longer chain hydrocarbons, particularly alkenes such as ethylene, produces a

product gas containing multiple byproducts, unreacted feedstock gases, and inert components in addition to ethylene. The ability to selectively and economically produce and separate methane based alkenes on a commercially viable scale provides a pathway to a significant new source of ethylene useful for production of ethylene based derivatives.

#### **BRIEF SUMMARY**

[0009] As noted above, the present disclosure is directed to methods for providing  $C_2$  carbon compounds via oxidative coupling of methane (OCM). The methods may be summarized as including steps of:

[0010] a) combining a feedstock gas comprising methane with an oxygen containing gas comprising oxygen;

[0011] (b) contacting the combined feedstock gas and oxygen containing gas with a catalyst and providing an OCM product gas comprising ethane and ethylene  $(C_2)$ ;

[0012] (c) compressing the OCM product gas;

[0013] (d) condensing at least a portion of the OCM product gas to provide an OCM product gas condensate comprising mostly water;

[0014] (e) introducing the OCM product gas condensate to a first separator;

[0015] (f) isentropically expanding and reducing the temperature of a first portion of the OCM product gas;

[0016] (g) introducing the first portion of the OCM product gas to the first separator and introducing a second portion of the OCM product gas to a second separator, the second separator operating at a lower pressure and temperature than the first separator;

[0017] (h) removing a C<sub>2</sub>-rich effluent and a methane/nitrogen containing gas mixture from the first separator;

[0018] (i) introducing the methane/nitrogen containing gas mixture to the second separator; and

[0019] (j) removing a methane-rich effluent and a nitrogen-rich effluent from the second separator.

[0020] In certain embodiments of the disclosed methods, the oxygen containing gas is compressed air having an oxygen content of about 21 mol % and a nitrogen content of about 78 mol %; and the nitrogen content in the methane/ nitrogen containing gas removed from the first separator may be at least about 85 mol %. In yet other embodiments, the first and second separators may operate at a below ambient temperature; and adiabatic expansion of at least one of the OCM product gas, a methane gas, a nitrogen gas, or a methane/nitrogen gas mixture may provide at least a portion of the cooling to produce the below ambient temperature. In other embodiments, the oxygen containing gas is compressed oxygen having an oxygen content of at least about 90 mol % and a nitrogen content of at most about 10 mol %; and the nitrogen content in the methane/nitrogen containing gas removed from the first separator may be at most about 85 mol %. In yet other embodiments, the first and second separators may operate at a below ambient temperature; and the compressed oxygen may be supplied via a cryogenic process and the cryogenic process may provide at least a portion of the cooling to produce the below ambient temperature.

[0021] Methods for providing C<sub>2</sub> carbon compounds via oxidative coupling of methane (OCM) in accordance with embodiments described herein may further include introducing at least a portion of the methane-rich effluent removed from the second separator to the feedstock gas prior to combining the feedstock gas with the oxygen

containing gas. In certain embodiments, the  $C_2$ -rich effluent may include at least about 90.0 mol %  $C_2$ , the methane-rich effluent may include at least about 92.0 mol % methane, and the nitrogen-rich effluent may include at least about 85.0 mol % nitrogen.

[0022] In other embodiments disclosed herein, methods for providing C<sub>2</sub> carbon compounds via oxidative coupling of methane (OCM) may further include reducing water content in the OCM product gas to about 0.001 mol % at most prior to condensing at least a portion of the OCM product gas.

[0023] Methods for providing C<sub>2</sub> carbon compounds via oxidative coupling of methane (OCM) in accordance with disclosed embodiments may further include reducing carbon dioxide content in the OCM product gas to about 5 ppm at most prior to condensing at least a portion of the OCM product gas.

[0024] Other embodiments of methods for providing C<sub>2</sub> carbon compounds via oxidative coupling of methane (OCM) may further include reducing hydrogen sulfide content in the feedstock gas to about 5 ppm. In certain embodiments disclosed herein, the feedstock gas may include at least about 20 mol % methane and compressing the OCM product gas may include increasing the pressure of the OCM product gas to at least about 100 pounds per square inch gauge (psig).

[0025] In another aspect of the disclosed subject matter processes for separating C<sub>2</sub> compounds from a product of an oxidative coupling of methane (OCM) process may be summarized as including:

[0026] (a) providing an OCM product gas from an OCM process, the OCM product gas comprising ethane and ethylene;

[0027] (b) compressing the OCM product gas to a pressure of at least about 200 pounds per square inch gauge (psig);

[0028] (c) reducing the temperature of the OCM product gas and condensing at least a portion of the OCM product gas to provide an OCM product gas condensate;

[0029] (d) separating the OCM product gas condensate from the OCM product gas;

[0030] (e) introducing the OCM product gas condensate to a first separator;

[0031] (f) separating the OCM product gas separated from the OCM product gas condensate into a first portion and a second portion and isentropically expanding the first portion of the OCM product gas through a turboexpander to reduce the temperature of the first portion of the OCM product gas;

[0032] (g) introducing the first portion of the OCM product gas to the first separator;

[0033] (h) removing a C<sub>2</sub>-rich effluent from the first separator;

[0034] (i) removing a first separator overhead gas from the first separator;

[0035] (j) reducing the temperature of the first separator overhead gas;

[0036] (k) introducing the cooled first separator overhead gas to a second separator;

[0037] (1) removing a methane-rich effluent from the second separator; and

[0038] (m) removing a nitrogen-rich effluent from the second separator.

[0039] In additional embodiments of the present disclosure, methods for separating  $C_2$  compounds from a product of an oxidative coupling of methane (OCM) process may further include:

[0040] (n) reducing the temperature of the second portion of the OCM product gas;

[0041] (o) adiabatically expanding the second portion of the OCM product gas to provide an at least partially condensed mixed stream that includes a second OCM product gas condensate and a second OCM product gas;

[0042] (p) introducing the at least partially flashed second OCM product gas condensate to the first separator; and

[0043] (q) reducing the temperature of the second OCM product gas and introducing the second OCM product gas to the second separator.

[0044] Methods for separating C<sub>2</sub> compounds from a product of an oxidative coupling of methane (OCM) process in accordance with disclosed embodiments of this aspect of the present disclosure may further include reducing water concentration in the OCM product gas to about 0.001 mole percent (mol %) at most and more preferably to about 0.0001 mol % (1 ppmv) at most prior to condensing at least a portion of the OCM product gas.

[0045] In other embodiments, methods for separating  $C_2$  compounds from a product of an oxidative coupling of methane (OCM) process may further include reducing carbon dioxide concentration in the OCM product gas to about 10 ppmv at most prior to condensing at least a portion of the OCM product gas.

[0046] In other embodiments, methods for separating  $C_2$  compounds from a product of an oxidative coupling of methane (OCM) process may further include reducing acetylene concentration in the OCM product gas to about 1 part per million by volume (ppmv) at most prior to condensing at least a portion of the OCM product gas or reducing the acetylene concentration in a  $C_2$ -rich effluent provided by the separations unit to about 1 ppmv at most.

[0047] In accordance with other disclosed embodiments of this aspect of the present disclosure, methods for separating C<sub>2</sub> compounds from a product of an oxidative coupling of methane (OCM) process may further include reducing hydrogen sulfide concentration in the OCM process to about 5 ppm at most using sulfur removal process, system and/or device, such as a sulfur trap. In other embodiments, providing the OCM product gas may include combining compressed air comprising oxygen and nitrogen and having an oxygen concentration of at least about 21 mol % with a feedstock gas comprising methane and having a methane concentration of at least 50 mol % and introducing the combined compressed air and feedstock gas to at least one OCM reactor. In other embodiments, the OCM product gas may include about 90 mol % or less nitrogen and providing the OCM product gas may include combining an oxygen containing gas comprising compressed oxygen and having an oxygen concentration of at least about 90 mol % with a feedstock gas comprising methane and having a methane concentration of at least about 50 mol % and introducing the combined compressed oxygen and feedstock gas to at least one OCM reactor. In certain embodiments, the OCM product gas may include about 10 mol % or less nitrogen.

[0048] In yet other embodiments, the method for separating C<sub>2</sub> compounds from a product of an oxidative coupling of methane (OCM) process disclosed herein may further include recycling at least a portion of the methane-rich

effluent from the second separator to an OCM reactor. In other embodiments, the  $C_2$ -rich effluent may include at least about 90 mol %  $C_2$ , the methane-rich effluent may include at least about 60 mol % methane, and the nitrogen-rich effluent may include at least about 50 mol % nitrogen.

[0049] In yet another aspect of the disclosed subject matter, processes for separating  $C_2$  compounds from a product of an oxidative coupling of methane (OCM) process may be summarized as including:

[0050] (a) combining a feedstock gas comprising methane with an oxygen containing gas;

[0051] (b) contacting the combined feedstock gas and oxygen containing gas with a catalyst and providing an OCM product gas having a C<sub>2</sub> concentration of from about 0.5 mol % to about 20 mol %, a methane content of about 60 mole percent (mol %) or less, and a nitrogen content of at least about 20 mol %;

[0052] (c) compressing the OCM product gas; and separating the OCM product gas into a  $C_2$ -rich effluent; a methane-rich effluent; and an nitrogen-rich effluent.

[0053] In accordance with embodiments of this aspect of the disclosed subject matter, separating the OCM product gas into the C<sub>2</sub>-rich effluent; the methane-rich effluent; and the nitrogen-rich effluent may occur at a lower than ambient temperature. In addition, in accordance with disclosed embodiments, adiabatic expansion of at least one of the OCM product gas, a methane gas, a nitrogen gas, or a methane/nitrogen gas mixture may provide at least a portion of the cooling to achieve the lower than ambient temperature and in other embodiments of the disclosed subject matter, adiabatic expansion of at least one of the OCM product gas, a methane gas, a nitrogen gas, or a methane/nitrogen gas mixture may provide all of the cooling to achieve the lower than ambient temperature.

[0054] In other embodiments, processes for separating  $C_2$  compounds from a product of an oxidative coupling of methane (OCM) process may further include recycling at least a portion of the methane-rich effluent and combining it with the feedstock gas and/or the oxygen containing gas. In other embodiments, the  $C_2$ + rich effluent may include at least about 90 mol %  $C_2$ + compounds, the methane-rich effluent may include at least about 60 mol % methane, and the nitrogen-rich effluent may include at least about 50 mol % nitrogen. In other embodiments, compressing the OCM product gas may include increasing the pressure of the OCM product gas to at least about 200 pounds per square inch gauge (psig).

[0055] In another aspect of the disclosed subject matter, processes for separating ethylene from a product of an oxidative coupling of methane (OCM) process may be summarized as including:

[0056] (a) reducing the hydrogen sulfide content of a feedstock gas comprising methane to about 5 ppm at most;

[0057] (b) combining the feedstock gas with an oxygen containing gas comprising oxygen;

[0058] (c) passing the combined feedstock gas and oxygen containing gas across a catalyst to provide an OCM product gas having an ethylene content of about 0.5 mol % or greater, a hydrogen content of from about 0.0 mol % to about 4.0 mol %, a methane content of about 95 mol % or less, and a nitrogen content of at least about 1 mol %;

[0059] (d) compressing the OCM product gas; and

[0060] (e) separating the OCM product gas into a ethylene-rich effluent; a methane-rich effluent; and an nitrogen-rich effluent.

[0061] In accordance with embodiments of this aspect of the disclosed subject matter, the OCM product gas exiting the OCM reactor may be at a temperature of no more than about 1750° F. (950° C.) or preferably no more than about 1650° F. (900° C.) and/or at a pressure of no more than 200 psig (690 kPa). In accordance with other embodiments, the catalyst may include a compound including at least one of an alkali metal, an alkaline earth metal, a transition metal, and a rare-earth metal.

[0062] In accordance with other embodiments, separating the OCM product gas into an ethylene-rich effluent; a methane-rich effluent; and a nitrogen-rich effluent may include:

[0063] (f) reducing the temperature of the OCM product gas and condensing at least a portion of the OCM product gas to provide an OCM product gas condensate;

[0064] (g) separating the OCM product gas condensate from the OCM product gas;

[0065] (h) introducing the OCM product gas condensate to a first separator;

[0066] (i) separating the OCM product gas separated from the OCM product gas condensate into a first portion and a second portion and isentropically expanding the first portion of the OCM product gas through a turboexpander to reduce the temperature of the first portion of the OCM product gas;

[0067] (j) introducing the first portion of the OCM product gas to the first separator;

[0068] (k) removing the ethylene-rich effluent from the first separator;

[0069] (1) removing a first separator overhead gas from the first separator;

[0070] (m) reducing the temperature of the first separator overhead gas;

[0071] (n) introducing the cooled first separator overhead gas to a second separator;

[0072] (o) removing the methane-rich effluent from the second separator; and

[0073] (p) removing the nitrogen-rich effluent from the second separator.

[0074] In accordance with other embodiments of this aspect of the present disclosure, processes for separating ethylene from a product of an oxidative coupling of methane (OCM) process may further include recycling at least a portion of the methane-rich effluent from the second separator to the reduced hydrogen sulfide content feedstock gas. In other embodiments, the nitrogen-rich effluent may include about 50 mole percent (mol %) or greater nitrogen concentration, the methane-rich effluent may include about 60 mol % or greater methane concentration, and the ethylene-rich effluent may include from about 10 mol % to about 60 mol % or greater ethylene concentration. In additional embodiments, separating the OCM product gas into the ethylene-rich effluent; the methane-rich effluent; and the nitrogen-rich effluent may occur at a lower than ambient temperature and adiabatic expansion of at least one of the OCM product gas, a methane gas, a nitrogen gas, or a methane/nitrogen gas mixture may provide at least a portion of the cooling to provide the lower than ambient temperature.

# BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0075] In the drawings, identical reference numbers identify similar elements or acts. The sizes and relative positions of elements in the drawings are not necessarily drawn to scale. For example, the shapes of various elements and angles are not drawn to scale, and some of these elements are arbitrarily enlarged and positioned to improve drawing legibility. Further, the particular shapes of the elements as drawn, are not intended to convey any information regarding the actual shape of the particular elements, and have been solely selected for ease of recognition in the drawings.

[0076] FIG. 1 is a block flow diagram depicting a methane based C<sub>2</sub> production and separation process, according to one illustrated embodiment;

[0077] FIG. 2 is a block flow diagram depicting a methane based C<sub>2</sub> production, treatment, and separation process, according to one illustrated embodiment;

[0078] FIG. 3 is a basic process flow diagram depicting a methane based  $C_2$  production and separation process, according to one illustrated embodiment;

[0079] FIG. 4 is a basic process flow diagram depicting a methane based  $C_2$  production, treatment and separation process, according to one illustrated embodiment;

[0080] FIG. 5 is a process flow diagram depicting a separation process useful for separating a mixed product gas stream resulting from a methane based C<sub>2</sub> production process, according to one illustrated embodiment;

[0081] FIG. 6 is a process flow diagram depicting another separation process useful for separating a mixed product gas stream resulting from a methane based C<sub>2</sub> production process, according to one illustrated embodiment;

[0082] FIG. 7 is a process flow diagram depicting a detail heat exchanging scheme of another separation process useful for separating a mixed product gas stream resulting from a methane based C<sub>2</sub> production process, according to one illustrated embodiment; and

[0083] FIG. 8 is a block flow diagram depicting another methane based  $C_2$  production and separation process, according to one illustrated embodiment.

#### DETAILED DESCRIPTION

[0084] In the following description, certain specific details are set forth in order to provide a thorough understanding of various disclosed embodiments. However, one skilled in the relevant art will recognize that embodiments may be practiced without one or more of these specific details, or with other methods, components, materials, etc. In other instances, well-known structures associated with specific unit operations, such as fluid transport, heat transfer, mass transfer, thermodynamic processes, and mechanical processes, e.g., fluid transportation, filtration, evaporation, condensation, gas absorption, distillation, extraction, adsorption, drying, gas liquefaction, and refrigeration have not been shown or described in detail to avoid unnecessarily obscuring descriptions of the embodiments.

[0085] Unless the context requires otherwise, throughout the specification and claims which follow, the word "comprise" and variations thereof, such as, "comprises" and "comprising" are to be construed in an open, inclusive sense, that is as "including, but not limited to."

[0086] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular

feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

[0087] As used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

[0088] As used in the specification and the appended claims, references are made to a "feedstock gas." It is understood that a feedstock gas may include any gas or gasified liquid containing methane and recognizable by one of ordinary skill in the art as being suitable for providing methane to a oxidative coupling of methane (OCM) reaction. As used in the specification and the appended claims, references are made to an "effluent." It is understood that an effluent may include any material or compound either removed or intended for removal from a particular location. Additionally, references are made to compositions that are variously described as being "nitrogen-rich," "methanerich," and "C<sub>2</sub>-rich." It should also be understood that the use of the suffix "-rich" indicates the compound or compounds having the greatest molar concentration within the composition. For example, a "nitrogen-rich effluent" describes an effluent where nitrogen has the greatest molar concentration. Similarly a "methane-rich gas" describes a gas where methane has the greatest molar concentration. As used in the specification and the appended claims, references are made to a "unit." It is understood that a unit may include any number of individual or combined unit operations such as separation, heating, cooling, condensation, vaporization, and the like as recognizable by one of ordinary skill in the art as being suitable or beneficial for achieving the indicated results. For example a "separation unit" may have more than one physical separator and may also include multiple ancillary heating, cooling, condensation and vaporization unit operations to achieve the desired separation.

[0089] As used herein the terms " $C_2$ " and " $C_2$  compounds" refer to alkane (i.e., ethane) and alkene (i.e., ethylene) hydrocarbons and not to alkyne (i.e., acetylene) hydrocarbons comprising 2 carbon atoms in their backbone. C2+ refer to 2 chain length hydrocarbons and higher hydrocarbon chain length comprising both alkanes and alkenes, e.g. propane and propylene. As used herein the term " $C_2$  content" refers to the concentration of  $C_2$  compounds (i.e., ethane+ethylene) present at the specified location.

[0090] The headings and Abstract of the Disclosure provided herein are for convenience only and do not interpret the scope or meaning of the appended claims or disclosed embodiments.

[0091] FIG. 1 is a block flow diagram depicting an illustrative C<sub>2</sub> production and separation process 100 including one or more oxidative coupling of methane (OCM) reactors 102 and one or more separation units 104. In process 100, the pressure of an oxygen containing gas 106 is increased, for example using one or more compressors 108, and the resultant higher pressure oxygen containing gas is combined with a feedstock gas 112 containing methane to provide a

feedstock gas/oxygen containing gas mixture 110. The feedstock gas/oxygen containing gas mixture 110 is introduced to the one or more OCM reactors 102. Within the one or more OCM reactors 102, methane present in the feedstock gas and the oxygen present in the oxygen containing gas are passed over a catalyst promoting the formation of an OCM product gas 114 including ethylene and ethane. The OCM product gas 114 may also contain amounts of unreacted feedstock such as methane; inert compounds such as nitrogen; and byproducts such as hydrogen, water vapor, and various carbon oxides (CO<sub>x</sub>).

[0092] In the embodiment of FIG. 1, the pressure of the OCM product gas 114 is increased, for example using one or more compressors 116 prior to introduction to the one or more separation units 104. Within the one or more separation units 104, at least three effluents are produced: a methane-rich effluent 120, a nitrogen rich effluent 122, and a C<sub>2</sub>-rich effluent **124**. At least a portion of the methane-rich effluent 120 may be recycled to the feedstock gas 112 or alternatively the methane-rich effluent 120 may not be recycled to the feedstock gas 112. Recycling of methanerich effluent 120 is beneficial since methane is the feedstock for the production of C<sub>2</sub>s, however recycling at least a portion of the methane-rich effluent 120 provides additional operational and economic benefits because the methane-rich effluent 120 can be utilized without having to meet the stringent requirements of a fungible product, for example a maximum nitrogen limit imposed on methane intended for injection into a natural gas transport or distribution systems. [0093] The C<sub>2</sub>-rich effluent 124 contains the desired ethane and ethylene compounds as well as C<sub>3</sub> and heavier hydrocarbon compounds such as propane and propylene (i.e.,  $C_{3+}$  compounds). In some instances the  $C_2$  compounds, particularly the ethylene, present in the C<sub>2</sub>-rich effluent **124** can be separated, for example using a C<sub>2</sub> splitter to selectively separate ethylene from ethane, and marketed as a commodity chemical. In other instances, all or a portion of the ethylene can be introduced to one or more additional unit operations, for example an oligomerization process to create oligomers, such as  $C_6$  (trimer) and  $C_8$  (tetramer) compounds, useful for example in liquid fuel products.

[0094] The oxygen containing gas 106 can include any source of oxygen such as air, purified oxygen, or mixtures thereof. The oxygen containing gas 106 can be an enriched oxygen containing gas sourced partially or wholly from an air separation plant or an air separation unit. The pressure of the oxygen containing gas 106 may be increased, for example using one or more compressors 108, to provide the higher pressure oxygen containing gas. In some embodiments, the temperature of the higher pressure oxygen containing gas can be adjusted, for example through the use of an intercooler and/or aftercooler installed and operated in conjunction with the one or more compressors 108. The addition of stoichiometric quantities of oxygen to the one or more OCM reactors via the oxygen containing gas 106 can limit the formation of undesirable combustion byproducts such as  $CO_x$  within the one or more OCM reactors 102. In some instances, the temperature of the oxygen containing gas 106 may be increased, for example by thermally contacting the oxygen containing gas 106 with one or more higher temperature gases or liquids, prior to mixing with the feedstock gas 112.

[0095] The composition of the oxygen containing gas 106 can vary dependent upon the source of the gas. For example,

where air is used to provide the oxygen containing gas, an oxygen content of about 21 mol % and a nitrogen content of about 78 mol % is provided. In at least some implementations, one or more inert gases, such as nitrogen, argon, or helium may be present in trace or larger quantities in the oxygen containing gas 106. Where purified oxygen is used to provide the oxygen containing gas, an oxygen content of greater than about 21 mol % is possible. The oxygen content of the oxygen containing gas 106 can be about 21 mol % or greater; about 40 mol % or greater; about 60 mol % or greater; or about 80 mol % or greater. Similarly, the nitrogen content of the oxygen containing gas 106 will vary dependent upon the source providing the oxygen containing gas **106**. The nitrogen content of the oxygen containing gas can be about 78 mol % or less; about 60 mol % or less; about 40 mol % or less; or about 20 mol % or less. In at least some implementations, the nitrogen content of the oxygen containing gas can be from about 5 mole percent (mol %) to about 95 mol %; about 10 mol % to about 90 mol %; about 15 mol % to about 85 mol %; about 20 mol % to about 80 mol %; or about 25 mol % to about 75 mol %. The pressure of the compressed oxygen containing gas 110 can vary. For example, the pressure of the compressed oxygen containing gas can be about 300 psig (2100 kPa) or less; about 200 psig (1400 kPa) or less; or more preferably about 100 psig (700 kPa) or less.

[0096] The feedstock gas 112 includes methane, all or a portion of which may include methane from relatively clean sources such as that available from a pipeline, commercial or industrial supply or distribution network. In some instances, all or a portion of the feedstock gas 112 may be sourced from so called "dirty" sources such as extracted natural gas that contains contaminants or impurities requiring removal prior to introducing the feedstock gas 112 to the one or more OCM reactors 102. While in general, the use of a feedstock gas 112 having a known, fixed methane composition is preferred, gases having a variable methane composition may also be used to provide all or a portion of the feedstock gas 112. Similarly, while the use of a feedstock gas 112 having a high methane content is preferred, gases having low methane content may also be used to provide all or a portion of the feedstock gas 112 provided any components detrimental to catalyst life, catalyst performance, or any components promoting undesirable side reactions or the formation of undesirable products are partially or completely removed prior to introducing the feedstock gas 112 to the one or more OCM reactors 102. The methane content of the feedstock gas 112 can vary and be about 20 mol % or less, about 35 mol % or less, about 50 mol % or less, about 80 mol % or less; about 90 mol % or less; about 95 mol % or less; or about 99 mol % or less.

[0097] Contaminants present in the feedstock gas 112 can include heavier weight hydrocarbons, acid gases such as carbon dioxide and hydrogen sulfide, nitrogen, water vapor, natural gas condensate ("casinghead gasoline"), and mercury to name a few. The feedstock gas 112 can be pretreated using known techniques prior to introduction to the one or more OCM reactors 102 to remove some or all of the contaminants such as hydrogen sulfide and heavier weight hydrocarbons that are capable of promoting the formation of undesired reaction side- or by-products, and/or detrimentally affecting the performance of the OCM catalyst disposed within the one or more OCM reactors 102. After treatment, the hydrogen sulfide content of the feedstock gas 112 can be

about 20 ppm or less; about 10 ppm or less; about 5 ppm or less; or about 1 ppm or less. After treatment the heavier weight hydrocarbons content of the feedstock gas 112 can be about 0.1 mol % or less; about 0.05 mol % or less; or about 0.01 mol % or less. Since the one or more OCM reactors 102 operate at an elevated temperature, the temperature of the feedstock gas 112 may be increased prior to mixing with the oxygen containing gas 106 to lessen the thermal input required to raise the temperature of the feedstock gas/oxygen containing gas mixture to the desired reaction temperature within the one or more OCM reactors 102.

[0098] In at least some embodiments the temperature and/or pressure of the feedstock gas 112 can be adjusted prior to mixing with the oxygen containing gas 106 or introduction to the one or more OCM reactors 102. The pressure and temperature of the feedstock gas 106 can vary. For example the pressure of the feedstock gas 112 can be about 150 psig (1035 kPa) or less; about 100 psig (690 kPa) or less; about 75 psig (520 kPa) or less; about 50 psig (345 kPa) or less; or about 30 psig (205 kPa) or less and the temperature of the feedstock gas 112 can be about 200° F. (93° C.) or less; about 150° F. (66° C.) or less; about 100° F. (38° C.) or about 30° F. (0° C.) or less.

[0099] The higher pressure oxygen containing gas may be introduced, mixed, or otherwise combined with the feedstock gas 112 either within the one or more OCM reactors 102 or prior to the entry of either, or both, the higher pressure oxygen containing gas and/or the feedstock gas 112 to the one or more OCM reactors 102. The feedstock gas/oxygen containing gas mixture 110 can be treated to remove one or more contaminants prior to introduction to the one or more OCM reactors 102. Contaminants present in the feedstock gas 112 may be detrimental to the OCM catalyst and/or the one or more OCM reactors 102 themselves and therefore the concentration of these contaminants is reduced prior to introducing the feedstock gas/oxygen containing gas mixture 110 to the one or more OCM reactors 102. For example, elemental sulfur or hydrogen sulfide may be present in concentrations ranging from trace amounts to double-digit mol % quantities within feedstock gas sources, such as extracted natural gas. The presence of sulfur or hydrogen sulfide can promote the formation of corrosive sulfurous acid within the one or more OCM reactors 102 and therefore are most desirably removed from the feedstock gas 112, oxygen containing gas 106 or the feedstock gas/oxygen containing gas mixture 110 prior to introducing the mixture to the one or more OCM reactors 102. After removal of sulfur or hydrogen sulfide, the hydrogen sulfide content of the feedstock gas/oxygen containing gas mixture 110 can be about 20 ppm or less; about 10 ppm or less; about 5 ppm or less; or more preferably about 1 ppm or less.

[0100] Additionally, the temperature of the feedstock gas/oxygen containing gas mixture 110 may be adjusted prior to introducing the mixture to the one or more OCM reactors 102. The temperature can be adjusted to a desired level to optimize the generation of preferred products such as ethylene within the one or more OCM reactors 102. In some instances, the temperature of the feedstock gas/oxygen containing gas mixture 110 may be adjusted in conjunction with one or more pretreatment steps, for example desulfurization of the feedstock gas/oxygen containing gas mixture 110. Prior to entering the one or more OCM reactors 102, the temperature of the feedstock gas/oxygen containing gas mixture 110 can be about 1300° F. (700° C.) or less; about

1110° F. (600° C.) or less; about 930° F. (500° C.) or less; about 750° F. (400° C.) or less; about 570° F. (300° C.) or less; or about 400° F. (200° C.) or less.

[0101] The OCM reactor 102 can include any vessel, device, system or structure capable of converting at least a portion of the feedstock gas/oxygen containing gas mixture 110 into one or more C<sub>2</sub> compounds using an oxidative coupling of methane process. The one or more OCM reactors 102 can be one or more similar or dissimilar reactors or reactor types arranged in series or parallel processing trains. The OCM process may be carried out in different types of commercially available reactors including a fixed bed reactor where the combined methane/oxygen gas mixture is passed through a structured bed; a fluidized bed reactor where the combined methane/oxygen mixture is used to fluidize a solid catalyst bed; and a membrane type reactor where the combined methane/oxygen mixture passes through an inorganic catalytic membrane.

[0102] The OCM reaction  $(2CH_4O_2 \rightarrow C_2H_4 + 2H_2O)$  is exothermic ( $\Delta H=-67$  kcals/mole) and generally requires very high temperatures (>700° C.). As a consequence, the OCM reactors 102 can be sized, configured, and/or selected based upon the need to dissipate the heat generated by the OCM reaction, for example in some embodiments, multiple, tubular, fixed bed reactors can be arranged in parallel to facilitate heat removal. In at least some embodiments, at least a portion of the heat generated within the one or more OCM reactors 102 can be recovered, for example the heat can be used to generate high pressure steam. Where colocated with processes requiring a heat input, at least a portion of the heat generated within the one or more OCM reactors 102 may be transferred, for example using a heat transfer fluid, to the co-located processes. Where no additional use exists for the heat generated within the one or more OCM reactors 102, the heat can be released to the atmosphere, for example using a cooling tower or similar evaporative cooling device.

[0103] In other embodiments, the one or more OCM reactors 102 may include multiple adiabatic, fixed-bed, OCM reactors arranged in a cascaded series, where the OCM product gas generated by a first OCM reactor is removed and introduced to a second OCM reactor, subsequent cascaded OCM reactors can be similarly arranged. In at least some embodiments, the OCM product gas removed from each reactor may be cooled, for example in a horizontal or vertical tube boiler using boiler feed water to generate high pressure steam, prior to introduction to a subsequent OCM reactor. A multi-stage, cascaded OCM reactor arrangement advantageously provides the ability to control the thermal profile through each OCM reactor and through the entire cascaded OCM reactor series. The ability to provide independent reactor thermal profiling as well as thermal profiling throughout all of the cascaded reactors can improve catalyst performance and catalyst life as well as providing a degree of product selectivity in the OCM product gas 114. [0104] In addition to a parallel configuration, multiple OCM reactors 102 may be arranged in a serial configuration or even a combination of series and parallel configurations. In a multiple reactor configuration, the OCM reactors 102 can be similar or different in size, type, or design based at least in part on process conversion and heat transfer specifications.

[0105] Chemical conversion is a measure of the quantity of reactants converted via a chemical reaction. Chemical

selectivity is a measure of the quantity of a reactant converted to the desired product. For example, within the one or more OCM reactors, in addition to the desired ethylene, methane in the feedstock gas 112 will also be converted to undesirable or unwanted byproducts including, but not limited to, water vapor, oxides of carbon, and hydrogen. The ethylene selectivity of the one or more OCM reactors 102 is therefore a quantitative measure of their ability to convert methane in the feedstock gas 112 to ethylene in the OCM product gas 114. Conversion and selectivity are dependent upon a multitude of factors, including but not limited to: reactor design, catalyst, and operating conditions.

[0106] Although other OCM catalysts can be disposed in at least a portion of the one or more OCM reactors 102, in at least some embodiments, at least a portion of the OCM catalyst in at least a portion of the one or more OCM reactors can include one or more nanowire-based OCM catalysts such as those developed by Siluria Technologies Inc. (Palo Alto, Calif.) and described in: U.S. patent application Ser. No. 13/115,082, filed May 24, 2011, entitled "Nanowire" Catalysts;" U.S. Provisional Patent Application Ser. 61/564, 832, filed Nov. 29, 2011, entitled "Catalysts for Petrochemical Catalysis;" U.S. Provisional Patent Application Ser. No. 61/564,834, filed Nov. 29, 2011, entitled "Nanowire Catalysts;" and U.S. Provisional Patent Application Ser. 61/564, 836, filed Nov. 29, 2011, entitled "Polymer Templated" Nanowire Catalysts", all of which are incorporated in their entirety by reference as if reproduced in their entirety herein. Using one or more nanowire based OCM catalysts within the one or more OCM reactors 102, the selectivity of the catalyst in converting methane to desirable C<sub>2</sub> products can be about 10% or greater; about 20% or greater; about 30% or greater; about 40% or greater; about 50% or greater; about 60% or greater; about 65% or greater; about 70% or greater; about 75% or greater; about 80% or greater; or about 90% or greater.

[0107] The one or more OCM reactors 102 provide an OCM product gas 114. Although variable based upon a multitude of process equipment, reactant and process conditions, the OCM product gas 114 can contain in addition to the desired and valued ethylene product: water vapor, methane, ethane, nitrogen, hydrogen, carbon oxides, small quantities of heavier hydrocarbons (hydrocarbons containing three or more carbon atoms), acetylene or inert compounds. In exemplary embodiments, the ethylene content of the OCM product gas 114 can be about 0.5 mol % or greater; about 1 mol % or greater; about 2 mol % or greater; about 5 mol % or greater; about or more preferably about 7 mol % or greater and the ethane content of the OCM product gas 114 can be about 0.5 mol % or greater; about 1 mol % or greater; about 2 mol % or greater; about 5 mol % or greater; or more preferably about 7 mol % or greater. In at least some implementations, one or more inert gases, such as nitrogen, argon, or helium may be present in trace or larger quantities in the OCM product gas 114.

[0108] Considerable quantities of nitrogen can be present in the OCM product gas 114, particularly where air is used to supply all or a portion of the oxygen containing gas 106. Nitrogen is carried through the one or more OCM reactors 102 as an inert compound and may therefore appear at a relatively high concentration in the OCM product gas 114. In contrast, the nitrogen content of the OCM product gas 114 can be relatively low when purified oxygen, for example oxygen supplied by an air separation unit, is used to provide

nearly all or all of the oxygen containing gas 106. In exemplary embodiments, the nitrogen content of the OCM product gas 114 can be about 1 mol % or less; about 5 mol % or less; about 40 mol % or less; or about 60 mol % or less. As discussed more fully below, the nitrogen or similar chemically inert gases in the OCM product gas 114 can be used advantageously in the separation unit 104 to provide some or all of the cooling required to recover C<sub>2</sub> compounds from the OCM product gas 114.

[0109] Hydrogen is liberated from the unsaturated hydrocarbons formed in the OCM reaction and may be present as a potential byproduct in the OCM product gas 114. The hydrogen content of the OCM product gas 114 can be about 4 mol % or less; about 3 mol % or less; about 2 mol % or less; or more preferably about 1 mol % or less.

[0110] Carbon oxides, including carbon monoxide and carbon dioxide, form as a result of the complete combustion of a portion of the hydrocarbons within the feedstock gas 112. Such combustion is an unintentional consequence of operating a high temperature hydrocarbon conversion process. In exemplary embodiments, the carbon oxide content of the OCM product gas 114 can be about 10 mol % or less; about 7 mol % or less; or more preferably about 5 mol % or less.

[0111] Within the one or more OCM reactors 102, the conversion of methane to heavier hydrocarbons is less than 100%. As a consequence, unreacted methane will be present in the OCM product gas 114. The quantity of methane within the OCM product gas will vary dependent upon the degree of conversion achieved within the one or more OCM reactors 102. In exemplary embodiments, the methane content of the OCM product gas 114 can be about 95 mole percent (mol %) or less; about 90 mol % or less; about 80 mol % or less; about 70 mol % or less; about 60 mol % or less; about 40 mol % or less; about 30 mol % or less; about 20 mol % or less; or about 10 mol % or less.

[0112] Where air is used to provide at least a portion of the oxygen containing gas 106, argon will accumulate due to the recycle of at least a portion of the non-condensable gas (principally nitrogen) from the separation unit 104 to the OCM reactors 102. In at least some situations, the argon content of the OCM product gas 110 can be 0 mol % for pure oxygen feed, about 1 mol % or less; about 5 mol % or less.

[0113] The temperature and pressure of the OCM product gas 114 is dependent upon maintaining a temperature and pressure profile within the one or more OCM reactors 102 that favors ethylene production while disfavoring the production of less desirable or undesirable by-products. Upon exiting the one or more OCM reactors 102, the OCM product gas 114 can be at a pressure of about 200 psig (1380) kPa) or less; about 150 psig (1035 kPa) or less; about 100 psig (690 kPa) or less; or more preferably about 50 psig (345 kPa) or less. Due to the exothermic nature of the OCM reaction, post-cooling, for example by passing the OCM product gas 114 across a boiler feedwater preheater proximate the one or more OCM reactors 102. In exemplary embodiments, upon exiting the one or more OCM reactors 102, the OCM product gas 114 can be at a temperature of about 1750° F. (950° C.) or less; about 1650° F. (900° C.) or less; about 1560° F. (850° C.) or less; about 1470° F. (800° C.) or less; about 1380° F. (750° C.) or less; about 1300° F. (700° C.) or less; about 1100° F. (590° C.) or less; about

900° F. (480° C.) or less; about 700° F. (370° C.) or less; or about 500° F. (260° C.) or less.

[0114] Upon exiting the one or more OCM reactors 102, the OCM product gas 114 is at a relatively high temperature and a relatively low pressure. Recalling that the presence of one or more inert gasses (e.g., nitrogen) within the OCM product gas 114 can be used advantageously to reduce the temperature within the separation unit 104, the pressure of the OCM product gas 114 may also be increased using the one or more compressors 116 to provide a compressed OCM product gas 118. The temperature of the OCM product gas 114 may be adjusted using one or more pre-coolers (not shown) prior to introducing the OCM product gas 114 to the one or more compressors 116. The temperature of the compressed OCM product gas 118 may be reduced using one or more inter- or after-coolers after introducing the OCM product gas 114 to the one or more compressors 116. After exiting the one or more compressors 116, in exemplary embodiments the temperature of the compressed OCM product gas 118 can be about 150° F. (65° C.) or less; about 125° F. (52° C.) or less; about 100° F. (38° C.) or less; or about 75° F. (24° C.) or less. After exiting the one or more compressors 116, in exemplary embodiments the pressure of the compressed OCM product gas 118 can be at least about 100 psig (690 kPa); at least about 150 psig (1035 kPa); at least about 200 psig (1380 kPa); at least about 250 psig (1725 kPa); or at least about 300 psig (2070 kPa).

[0115] The compressed OCM product gas 118 may be introduced to the separation unit 104. Within the separation unit 104, the mixed gasses within the compressed OCM product gas 118 are separated to provide the methane rich effluent 120, the nitrogen rich effluent 122, and the  $C_2$ -rich effluent 124. In at least some embodiments, the separation unit can use in whole or in part, a cryogenic separation process to provide the methane rich effluent 120, the nitrogen rich effluent 121, and the  $C_2$ -rich effluent 121.

[0116] Acetylene may be present in the OCM product gas at concentrations of up to about 0.1 mole percent (mol %); about 0.2 mol %; about 0.3 mol %; about 0.4 mol %; about 0.5 mol %; or about 0.75 mol %. All or a portion of any acetylene present in the OCM product gas 114 may be removed from the OCM product gas 114. In at least some instances, at least a portion of any acetylene present in the OCM product gas 114 may be converted to at least one more preferable chemical species. For example, at least a portion of any acetylene present in the OCM product gas 114 may be converted to ethylene by passing all or a portion of the OCM product gas 114 through an acetylene reactor where the acetylene is catalytically, selectively, hydrogenated. In another implementation, at least a portion of any acetylene present may be fully hydrogenated to provide ethane. In yet another implementation, at least a portion of any acetylene present may be removed from the OCM product gas 114 and destroyed, for example via thermal combustion or oxidation in a controlled environment or via flare.

[0117] The gases in at least a portion of the compressed OCM product gas 118 may be adiabatically expanded to provide at least a portion of the cooling used in the cryogenic processes within the separation unit 104. In some embodiments, at least a portion of the gasses within the separation unit 104 may be recompressed and re-adiabatically expanded to provide additional cooling and, potentially, obviate the need for external refrigeration within the separation unit 104. Additionally, in some instances, at least a

portion of the gasses within the separation unit 104 may be isentropically expanded, for example using a turboexpander, to provide mechanical work (e.g., a shaft output) useful within the separation unit 104.

[0118] Within the separation unit 104, heavier hydrocarbon compounds, including ethane and ethylene are separated from the OCM product gas 118 to provide the C2-rich effluent 124 and a mixed nitrogen/methane containing gas. In some implementations, any acetylene present in the OCM product gas 118 may be at least partially removed using one or more systems, devices, or processes included in the separation unit 104. In other implementations, any acetylene present in the OCM Product gas 118 may be at least partially converted to one or more preferable chemical species using one or more systems, devices, or processes included in the separation unit 104. For example, all or a portion of the OCM product gas 118 or the C2-rich effluent 124 may be passed through an acetylene reactor where at least a portion of the acetylene present in the OCM product gas 118 or the C<sub>2</sub>-rich effluent **124** is selectively, catalytically hydrogenated to ethylene. Such acetylene removal or conversion may occur at any point in the separation unit 104, including preparatory to performing any separations (e.g., removal from the OCM product gas 118), after completion of the separations (e.g., removal from the  $C_2$ -rich effluent 124), at an intermediate stage of the separations process, or any combination thereof.

[0119] The mixed nitrogen/methane containing gas can be separated in separation unit to provide the nitrogen-rich effluent 122 and the methane-rich effluent 120. At least a portion of the methane-rich effluent 120 can be recycled back to the feedstock gas 112 or to the one or more OCM reactors 102. The methane-rich effluent 120 consists primarily of methane with other compounds present in small quantities. In exemplary embodiments, the methane content of the methane-rich effluent 120 can be about 60 mole percent (mol %) or greater; 80 mol % or greater; about 85 mol % or greater; about 90 mol % or greater; or more preferably about 95 mol % or greater. As explained above, the quantity and the concentration of nitrogen in the nitrogen-rich effluent 122 can depend upon the source used to supply the oxygen containing gas 106. In exemplary embodiments, the nitrogen content of the nitrogen-rich effluent 122 can be about 50 mol % or greater; about 75 mol % or greater; about 85 mol % or greater; or more preferably about 90 mol % or greater. The C<sub>2</sub>-rich effluent **124** contains ethane, ethylene, and higher molecular weight hydrocarbons. In exemplary embodiments, the ethane content of the C<sub>2</sub>-rich effluent **124** can be about 10 mol % or greater; about 20 mol % or greater; about 30 mol % or greater; about 40 mol % or greater; about 50 mol % or greater; or more preferably about 60% or greater and the ethylene content of the C<sub>2</sub>-rich effluent **124** can be about 10 mol % or greater; about 20 mol % or greater; about 30 mol % or greater; about 40 mol % or greater; about 50 mol % or greater; or more preferably about 60 mol % or greater.

[0120] FIG. 2 is a block flow diagram depicting an illustrative C<sub>2</sub> production and separation process 200 having one or more oxidative coupling of methane (OCM) reactors 102, one or more separation units 104, and one or more pretreatment units 202 are useful in removing contaminants and other undesirable compounds from the compressed OCM product gas 118 to provide a cleaned, compressed, OCM product gas 204. For

example, water and carbon dioxide, both of which can freeze during a cryogenic process within the one or more separation units 104 may be removed from the compressed OCM product gas 118 in one or more pretreatment units 202. Although depicted as a single entity in FIG. 2, the one or more pretreatment units 202 can include multiple unit operations each targeting the reduction of the amount of one or more contaminants present within the compressed OCM product gas 118.

[0121] The compressed OCM product gas 118 can be introduced to the one or more pretreatment units 202 to remove one or more undesired components present in the compressed OCM product gas 118. For example, all or a portion of the carbon dioxide present within the compressed OCM product gas 118 can be removed within the one or more pretreatment units 202. Numerous methods of reducing the amount of carbon dioxide within the compressed OCM product gas 118 may be used. For example, the carbon dioxide level within the compressed OCM product gas 118 may be reduced by contacting the compressed OCM product gas 118 with a solution containing one or more amines such as monoethanolamine (MEA). In at least some embodiments at least a portion of the steam produced as a byproduct from the one or more OCM reactors can be used to facilitate the removal of carbon dioxide 206 from the compressed OCM gas 118 to provide the cleaned, compressed OCM product gas 204. For example, byproduct steam may be useful in the thermal regeneration of caustic that has been converted to calcium carbonate in a carbon dioxide scrubber. In exemplary embodiments, the carbon dioxide content of the cleaned, compressed OCM product gas **204** can be about 20 ppm or less; about 10 ppm or less; or more preferably about 5 ppm or less.

[0122] Additionally, all or a portion of the water 208 present in the compressed OCM gas 118 as a water vapor can be removed within the one or more pretreatment units 202. Numerous methods of reducing water vapor levels within the compressed OCM product gas 118 may be used. For example, the amount of water in the form of water vapor within the compressed OCM product gas 118 may be reduced using a thermal swing adsorption (TSA) process such as a multi-column TSA process enabling continuous water vapor removal and adsorbent bed regeneration. In at least some embodiments at least a portion of the steam produced as a byproduct from the one or more OCM reactors can be used to facilitate the regeneration of the adsorbent beds within a TSA process. In exemplary embodiments, the water vapor content of the cleaned, compressed OCM product gas 204 can be about 0.05 mol % or less; about 0.01 mol % or less; or more preferably about 0.001 mol % or less.

[0123] In at least some implementations, the pretreatment unit 202 may include one or more systems, devices, or processes to optionally remove at least a portion of any acetylene present in the OCM product gas 118. In other implementations, the pretreatment unit 202 may include one or more systems, devices, or processes to optionally convert at least a portion of any acetylene present in the OCM product gas 118 to one or more preferred chemical species. For example, in at least some implementations, all or a portion of the OCM product gas 118 may be passed through an acetylene reactor where at least a portion of the acetylene present in the OCM product gas 118 can be selectively, catalytically hydrogenated to ethylene.

[0124] FIG. 3 is a basic process flow diagram depicting a methane based C<sub>2</sub> production and separation process 300 including a first separator 302 providing the C<sub>2</sub>-rich effluent 124 and a methane/nitrogen gas and a second separator 304 providing the methane-rich effluent 124 and the nitrogenrich effluent 122. In the embodiment illustrated in FIG. 3, the temperature of the compressed OCM product gas 118 is reduced using one or more heat exchangers 306. The temperature of the compressed OCM product gas 118 may be lowered through the use of an external cooling media, a relatively cool process stream, or combinations thereof. Reducing the temperature of the OCM product gas 118 will condense at least a portion of the higher boiling point components in the compressed OCM product gas 118, including at least a portion of the C<sub>2</sub> and heavier hydrocarbons present in the compressed OCM product gas 118.

[0125] At least a portion of the condensed high boiling point components can be separated from the compressed OCM product gas 118 using one or more liquid/gas separators, such as knockout drums 308 to provide an OCM product gas condensate 310 and a compressed OCM product gas 312. The OCM product gas condensate 310 is introduced to the first separator 302 and at least a portion 314 of the compressed OCM product gas 312 can be introduced to one or more turboexpanders **316**. The isentropic expansion of the compressed OCM product gas 314 within turboexpanders 316 can produce shaft work useful for driving one or more compressors or other devices in the separation unit 104. The isentropic expansion of the compressed OCM product gas 314 with the turboexpanders reduces the temperature of the compressed OCM product gas 318 that exits from the one or more turboexpanders. The compressed OCM product gas 318 from the one or more turboexpanders 316 is introduced to the first separator 302.

[0126] The first separator 302 can be any system, device or combination of systems and devices suitable for promoting the separation of  $C_2$  and heavier hydrocarbons from a gas stream comprising mainly nitrogen and methane. For example, cryogenic distillation at a relatively high temperature may be used to promote the separation of C<sub>2</sub> and heavier hydrocarbons from a gas comprising mainly nitrogen and methane. The  $C_2$ -rich effluent **124** is withdrawn from the first separator 302 and a mixed nitrogen/methane containing gas mixture 320 is also withdrawn from the first separator **302**. The nitrogen content of the nitrogen/methane containing gas mixture 320 withdrawn from the first separator 302 can be about 95 mol % or less; about 85 mol % or less; about 75 mol % or less; about 55 mol % or less; about 30 mol % or less. The balance of the nitrogen/methane gas mixture 320 comprises principally methane with small quantities of hydrogen, carbon monoxide, and inert gases such as argon. [0127] In at least some embodiments, the first separator 302 may be referred to as a "demethanizer" based on its ability to separate methane from C<sub>2</sub> and higher hydrocarbons. An exemplary first separator 302 is provided by a vertical distillation column operating at below ambient temperature and above ambient pressure. The operating temperature and pressure within the first separator 302 can be established to improve the recovery of the desired C<sub>2</sub> hydrocarbons in the  $C_2$ -rich effluent 124. In exemplary embodiments, the first separator 302 can have an overhead operating temperature of from about -260° F. (-162° C.) to about -180° F. (-118° C.); about -250° F. (-157° C.) to about -190° F. (-123° C.); about -240° F. (-151° C.) to

about -200° F. (-129° C.); or more preferably from about -235° F. (-148° C.) to about -210° F. (-134° C.) and an bottom operating temperature of from about -150° F. (-101° C.) to about -50° F. (-46° C.); about -135° F. (-93° C.) to about -60° F. (-51° C.); from about -115° F. (-82° C.) to about -70° F. (-57° C.); or more preferably about -100° F. (-73° C.) to about -80° F. (-62° C.). In exemplary embodiments, the first separator 302 can be at an operating pressure of from about 30 psig (205 kPa) to about 130 psig (900 kPa); about 40 psig (275 kPa) to about 115 psig (790 kPa); about 50 psig (345 kPa) to about 95 psig (655 kPa); or more preferably about 60 psig (415 kPa) to about 80 psig (550 kPa).

[0128] The temperature of at least a portion of the C<sub>2</sub>-rich effluent 124 from first separator 302 can be increased in one or more heat exchangers 322 using a heat transfer fluid, a warm process flow stream, or a combination thereof. The one or more heat exchangers 322 can include any type of heat exchange device or system including, but not limited to one or more plate and frame, shell and tube, or the like. After exiting the one or more heat exchangers 322, in exemplary embodiments, the temperature of the C<sub>2</sub>-rich effluent 124 can be about 50° F. (10° C.) or less; about 25° F. (-4° C.) or less; about 0° F. (-18° C.) or less; about -25° F. (-32° C.) or less; or about -50° F. (-46° F.) or less and the pressure can be about 130 psig (900 kPa) or less; about 115 psig (790 kPa) or less; about 80 psig (550 kPa) or less.

[0129] The temperature of the nitrogen/methane containing gas mixture 320 withdrawn from the first separator 302 can be lowered in one or more heat exchangers 324 using one or more refrigerants, one or more relatively cool process flows, or combinations thereof. The one or more heat exchangers 324 can include any type of heat exchange device or system including, but not limited to one or more plate and frame, shell and tube, or the like. The cooled nitrogen/methane gas mixture 320 exiting one or more heat exchangers 324 is introduced to the second separator 304.

[0130] In some embodiments a portion 326 of the OCM product gas 312 removed from the knockout drum 308 and not introduced to the one or more turboexpanders 316 can be cooled using one or more heat exchangers 328. The one or more heat exchangers 328 can include any type of heat exchange device or system including, but not limited to one or more plate and frame, shell and tube, or the like. The temperature of the portion 326 of the OCM product gas 312 can be decreased using one or more refrigerants, one or more relatively cool process flows, or combinations thereof. The cooled portion 326 of the OCM product gas 312, containing a mixture of nitrogen and methane is introduced to the second separator 304.

[0131] The second separator 304 can be any system, device or combination of systems and devices suitable for promoting the separation of methane from nitrogen. For example, cryogenic distillation at a relatively low temperature can be used to promote the separation of methane from nitrogen in a gas stream. Conditions within the second separator 304 promote the condensation of methane and the separation of liquid methane from the gaseous nitrogen within the second separator 304. The liquid methane containing methane-rich effluent 120 is withdrawn as a liquid from the second separator 304 and the nitrogen-rich effluent 122 is withdrawn as a gas from the second separator 304. An exemplary second separator 304 is provided by a vertical

distillation column operating significantly below ambient temperature and above ambient pressure. The operating temperature and pressure within the second separator 302 can be established to improve the separation of liquid methane as the methane-rich effluent 120 from the gaseous nitrogen as the nitrogen-rich effluent 122. For example, the second separator 304 can have an overhead operating temperature of from about -340° F. (-210° C.) to about -240° F. (-151° C.); about -330° F. (-201° C.) to about -250° F. (-157° C.); about -320° F. (-196° C.) to about -260° F. (162° C.); about -310° F. (-190° C.) to about -270° F. (-168° C.); or more preferably about -300° F. (-184° C.) to about -280° F. (-173° C.) and a bottom operating temperature of from about  $-280^{\circ}$  F.  $(-173^{\circ}$  C.) to about  $-170^{\circ}$  F. (-112° C.); about -270° F. (-168° C.) to about -180° F. (-118° C.); about -260° F. (-162° C.) to about -190° F. (-123° C.); about -250° F. (-159° C.) to about -200° F. (-129° C.); or more preferably about -240° F. (-151° C.) to about -210° F. (-134° C.). In exemplary embodiments, the second separator 304 can be at an operating pressure of from about 85 psig (585 kPa) or less; about 70 psig (480 kPa) or less; about 55 psig (380 kPa) or less; or more preferably about 40 psig (275 kPa) or less.

[0132] The temperature of at least a portion of the methane-rich effluent 120 from the second separator 304 can be increased using one or more heat exchangers 330. In at least some instances, one or more compressors may be used to increase the pressure and temperature of the methane-rich effluent 120 from the second separator 304 prior to recycling at least a portion of the compressed methane-rich effluent 304 to the feedstock gas/oxygen containing gas mixture 110. The one or more heat exchangers 330 can include any type of heat exchange device or system including, but not limited to one or more plate and frame, shell and tube, or the like. The temperature of the methane-rich effluent 120 may be increased in heat exchangers 330 using a heat transfer fluid, a warm process flow, or a combination thereof. After exiting the one or more heat exchangers 330, in exemplary embodiments the temperature of the methane-rich effluent 120 can be about 125° F. (52° C.) or less; about 100° F. (38° C.) or less; or more preferably about 90° F. (32° C.) or less and the pressure of the methane-rich effluent 120 can be about 150 psig (1035 kPa) or less; about 100 psig (690 kPa) or less; or more preferably about 50 psig (345 kPa) or less. In an embodiment in accordance with FIG. 3, at least a portion of the methane-rich effluent 120 can be recycled to the feedstock gas 112, the feedstock gas/oxygen containing mixture 110, the compressed oxygen containing gas, or to the one or more OCM reactors 102.

[0133] The temperature of at least a portion of the nitrogen-rich effluent 122 can be increased using one or more heat exchangers 332. The one or more heat exchangers 332 can include any type of heat exchange device or system including, but not limited to one or more plate and frame, shell and tube, or the like. The temperature of the nitrogen-rich effluent 122 may be increased in heat exchangers 332 using a heat transfer fluid, a warm process flow, or a combination thereof. After exiting the one or more heat exchangers 332, in exemplary embodiments, the temperature of the nitrogen-rich effluent 122 can be about 125° F. (52° C.) or less; about 100° F. (38° C.) or less; or more preferably about 90° F. (32° C.) or less and the pressure of the nitrogen-rich effluent 122 can be about 150 psig (1035).

kPa) or less; about 100 psig (690 kPa) or less; or more preferably about 50 psig (345 kPa) or less.

[0134] Although described above for brevity and clarity as independent heat exchange devices, the one or more heat exchangers 306, 322, 324, 328, 330, and 332 may be integrated into one or more composite heat exchange devices permitting, where appropriate, heat exchange between process flows of differing temperatures.

[0135] FIG. 4 is a basic process flow diagram depicting a methane based C<sub>2</sub> production and separation process 400 including compressed OCM product gas 114 pretreatment, a first separator 302 providing the C<sub>2</sub>-rich effluent 124 and a methane/nitrogen gas and a second separator 304 providing the methane-rich effluent 124 and the nitrogen-rich effluent **122**. In some embodiments, the compressed OCM product gas 114 can be introduced to a carbon dioxide removal treatment system 402. Carbon dioxide removal treatment system can comprise systems suitable for removing carbon dioxide from OCM product gas 114. In some embodiments, an ethanolamine-based carbon dioxide removal process can be used to scrub carbon dioxide from the compressed OCM product gas 114. The spent ethanolamine solution can be regenerated via heating thereby providing a recyclable carbon dioxide scrubbing solution. In other embodiments, a caustic-based carbon dioxide removal process can be used to scrub carbon dioxide from the compressed OCM product gas 114. In some instances, the sodium carbonate formed by scrubbing the carbon dioxide from the compressed OCM product gas 114 can be reacted with calcium hydroxide to form calcium carbonate and regenerate the caustic for recycle to the carbon dioxide removal treatment system 402. [0136] The compressed OCM product gas 114 can also be introduced to a water removal system 404 that includes systems for removing water from OCM product gas 114. In some embodiments, the water removal system can include a thermal swing adsorption (TSA) system having at least two TSA columns to provide continuous water removal capability. Further details of exemplary TSA water removal systems have been described above.

[0137] FIG. 5 is a process flow diagram depicting a separation process 500 useful within one or more separation units 104 to separate the cleaned, compressed OCM product gas 204, according to one illustrated embodiment. As depicted in FIG. 5, heat exchange between various process streams is used to provide process heating and cooling as needed. Importantly, the adiabatic expansion of one or more process gasses coupled with the use of process heat exchange can minimize or even eliminate the requirement for the supply of external refrigeration to the separation process 500. In some instances, for example where purified or separated oxygen provides at least a portion of the oxygen containing gas 106, insufficient gas volume within the separation unit 104 may serve to limit the cooling effect realized by the adiabatic expansion of process gas within the separation unit 104. In such embodiments, external cooling, for example cooling from a cryogenic process providing the oxygen containing gas 106 may be used to provide at least a portion of the cooling within the separation unit 104.

[0138] In at least some embodiments, the pressure of the methane-rich effluent 120 withdrawn from the second separator 304 may be adjusted to provide a methane-rich effluent at two or more pressures. Such an arrangement may be advantageous for example, when a first portion 502 of the methane-rich effluent 120 is intended for distribution within

a commercial or industrial distribution network operating at a relatively low pressure and a second portion **504** of the methane-rich effluent **120** is intended for injection into a transport pipeline operating at a relatively high pressure. For example, the pressure of the first portion **502** of the methane-rich effluent **120** may be reduced to a pressure of from about 5 psig (35 kPa) to about 30 psig (205 kPa) by passing portion **502** of the methane-rich effluent **120** through a pressure reduction device such as a pressure reducing valve **506**. The pressure of the second portion **504** of the methane-rich effluent **120** may be increased to a pressure of from about 30 psig (205 kPa) to about 100 psig (690 kPa) by passing portion **504** of the methane-rich effluent **120** through a pressure increasing device such as a fluid mover **508**.

[0139] The cleaned, compressed OCM product gas 204 is introduced to the separation process 500. Recall, the OCM product gas exiting the one or more OCM reactors 102 is at an elevated temperature. While the OCM product gas is cooled, the temperature of the OCM product gas entering the separation process 500 remains at a relatively warm temperature, for example between about 50° F. (10° C.) and 150° F. (66° C.). Conversely, the C<sub>2</sub>-rich effluent **124** withdrawn from the first separator 302 is typically at a relatively cool temperature, for example between about -150° F. (-101° C.) and about -80° F. (-62° C.). The first and second portions 502, 504 of the methane-rich effluent 120 and the nitrogen-rich effluent 122 withdrawn from the second separator 304 are also typically at relatively cool temperatures, for example between -340° F. (-207° C.) and about -170° F. (-112° C.). By thermally contacting the relatively warm cleaned, compressed OCM product gas 204 with the relatively cool C<sub>2</sub>-rich effluent **124**, first and second portions 502, 504 of the methane-rich effluent 120 and the nitrogen-rich effluent 122 in a first heat exchange device 510, the temperature of the cleaned, compressed OCM product gas 204 can be decreased and the temperature of the effluent streams increased. The first heat exchange device 510 can be any type, size, or shape heat exchange device capable of transferring heat between three or more components.

[0140] Recall from FIG. 3 the OCM product gas 312 removed from the knockout drum 308 can be apportioned or otherwise separated into a first portion 314 that is introduced to the one or more turboexpanders 316 and a second portion 326 that is ultimately introduced to the second separator 304. The adiabatic expansion of the cleaned, compressed OCM product gas 204 within the knockout drum 308 reduces the temperature of the OCM product gas 312 exiting drum 308. Thus, the temperature of the second portion of the OCM product gas 326 will be at a lower temperature than the cleaned, compressed OCM product gas 204 entering knockout drum 308.

[0141] By thermally contacting the relatively warm cleaned, compressed OCM product gas 204 and the second portion of the OCM product gas 326 with the relatively cool first and second portions 502,504 of the methane-rich effluent 120 and the nitrogen-rich effluent 122 in a second heat exchange device 512, the temperature of the cleaned, compressed OCM product gas 204 and the second portion of the OCM product gas 326 can be further decreased and the temperature of the effluent streams increased. The second heat exchange device 512 can be any type, size, or shape heat exchange device capable of transferring heat between three or more components.

[0142] Cooling the second portion of the OCM product gas 326 can form a second OCM product gas condensate within the second portion of the OCM product gas 326. The second portion of the OCM product gas 326 can be introduced to a liquid/gas separation device, such as a knockout drum 514 where the second OCM product gas condensate 516 is removed and returned to the first separator 302, for example as a reflux to the first separator 302. The OCM product gas 518 is withdrawn from the drum 514 and introduced to the second separator 304.

[0143] In some embodiments, by thermally contacting the relatively warm OCM product gas 518 and the nitrogen/methane gas mixture 320 withdrawn from the first separator 302 with the relatively cool first and second portions 502, 504 of the methane-rich effluent 120 and the nitrogen-rich effluent 122 from second separator 304 in a third heat exchange device 520, the temperature of the OCM product gas 518 and the nitrogen/methane gas mixture 320 can be further decreased and the temperature of the effluent streams increased. The third heat exchange device 512 can be any type, size, or shape heat exchange device capable of transferring heat between three or more components.

[0144] In at least some embodiments, the pressure of the  $C_2$ -rich effluent 124 withdrawn from the first separator 302 can be increased, for example through the use of one or more fluid movers 522. The  $C_2$ -rich effluent 124 contains a mixture of ethane, ethylene and heavier hydrocarbons such as propane, butane, pentane and hexane. In at least some embodiments, all or a portion of the  $C_2$ -rich effluent 124 can be fractionated or otherwise separated, for example within a  $C_2$  separation process or column (e.g. a "de-ethanizer") to provide at least an ethylene-rich effluent and an ethane-rich effluent. The ethylene-rich effluent can provide either a feedstock to a subsequent process or a fungible product. All or a portion of the ethane may be recycled back to the feedstock gas 112.

[0145] FIG. 6 is a process flow diagram depicting another separation process 600 within one or more separation units 104 to separate the cleaned, compressed OCM product gas 204 into desired fractions, according to one illustrated embodiment. As depicted in FIG. 6, in addition to heat exchange between various process streams to provide process heating and cooling as needed, heat exchange is also useful for providing one or more reboiler loops (i.e., thermal energy inputs) to the first separator 302 and the second separator 304. Additionally, the nitrogen/methane gas mixture 320 from the first separator 302 and the OCM product gas 518 from knockout drum 514 may also provide one or more thermal contributions to the third heat exchanger 520. [0146] In at least some embodiments, the OCM product gas 518 withdrawn from the knockout drum 514 is introduced to a second knockout drum 602. Non-condensed OCM product gas **604** is withdrawn from the second knockout drum 602. The temperature of the OCM product gas 604 can be reduced in the third heat exchanger 520 prior to introducing the OCM product gas 604 to the second separator 304. Any OCM product gas condensate 606 in the second knockout drum 602 is withdrawn and introduced to a third knockout drum 608.

[0147] In at least some embodiments, the nitrogen/methane gas mixture 320 can be withdrawn from the first separator 302 and introduced to the third heat exchanger 520 where a portion of the nitrogen/methane gas mixture 320 can condense. Any condensate present in either or both the

nitrogen/methane gas mixture 320 and the OCM product gas condensate 606 are separated in the third knockout drum 608. The gas 610 within the third knockout drum 608, comprising the nitrogen/methane gas mixture 320 and any OCM product gas from the OCM product gas condensate 606 are withdrawn from the third knockout drum 608. The temperature of the relatively warm gas 610 is increased using the third heat exchanger 520 prior to introducing the gas 610 to the second separator 304. Similarly, relatively warm condensate 612 from the third knockout drum 608 is withdrawn from the drum 608 and the temperature of the condensate 612 increased using the third heat exchanger 520 prior to introducing the condensate 612 to the second separator 304.

[0148] In some embodiments, the thermal efficiency of the separation unit 104 may be improved by the transfer of thermal energy (i.e. heat) from the first heat exchanger 510 and the second heat exchanger 512 to the first separator 302 via reboiler loops 614 and 616, respectively. Similarly, additional thermal efficiency may be realized by the transfer of thermal energy (i.e. heat) from the third heat exchanger 520 to the second separator 304 via reboiler loop 618. In some embodiments, the thermal energy may be transferred between the heat exchangers and the separators using a closed loop heat transfer fluid. In other embodiments, the liquid present in the separator may be withdrawn and passed through the respective heat exchanger. In yet other embodiments, a portion of the first and second heat exchangers 510, 512 may be partially or completely disposed within the first separator 302 and a portion of the third heat exchanger 520 may be partially or completely disposed within the second separator 304.

[0149] The process flow diagram shown in FIG. 7 provides a more detailed breakdown of the thermal conservation process 700 that occurs in the first heat exchanger 510, the second heat exchanger 512, and the third heat exchanger **520**, according to one implementation. The thermal transfer processes occurring in each of the first heat exchanger 510, the second heat exchanger 512, and the third heat exchanger **520** are described in greater detail in Tables 1, 2, and 3 that follow. In the following tables, the term "hot stream" refers to a gas, liquid, or combination thereof whose thermal energy or temperature decreases as the gas, liquid, or combination thereof passes through the heat exchanger. In the following tables, the term "cold stream" refers to a gas, liquid, or combination thereof whose thermal energy or temperature increases as the gas, liquid, or combination thereof passes through the heat exchanger. For convenience and ease of description, each of heat exchangers 510, 512, and 520 are broken into a number of thermal cells in the following tables. One of ordinary skill in the chemical engineering art would readily appreciate that such cells may be freely added, removed or changed between heat exchangers to provide alternate levels of thermal conservation provided by the thermal conservation process 700. Although only one cold stream and one hot stream are shown as included in each thermal cell, one of ordinary skill in the chemical engineering arts would readily appreciate that more than two streams (e.g., one hot stream and two cold streams, etc.) could be readily passed through a single thermal cell.

TABLE 1

HEAT EXCHANGER 510 THERMAL CELLS						
Cell ID	#	Cold Gas/Liquid	#	Hot Gas/Liquid		
710a 710b 710c 710d 710e	122 502 504 124 614	Nitrogen rich effluent  1 <sup>st</sup> methane rich effluent  2 <sup>nd</sup> methane rich effluent  C <sub>2</sub> -rich effluent  302 Reboiler loop	204 204 204 204 204	OCM product gas		

TABLE 2

HEAT EXCHANGER 512 THERMAL CELLS					
Cell ID	#	Cold Gas/Liquid	#	Hot Gas/Liquid	
712a	122	Nitrogen rich effluent	204	OCM product gas	
712b	502	1 <sup>st</sup> methane rich effluent	204	OCM product gas	
712c	504	2 <sup>nd</sup> methane rich effluent	204	OCM product gas	
712d	616	302 Reboiler loop	204	OCM product gas	
712e	122	Nitrogen rich effluent	326	OCM product gas fraction	
712f	502	1 <sup>st</sup> methane rich effluent	326	OCM product gas fraction	
712g	504	2 <sup>nd</sup> methane rich effluent	326	OCM product gas fraction	

TABLE 3

HEAT EXCHANGER 520 THERMAL CELLS						
Cell ID	#	Cold Gas/Liquid	#	Hot Gas/Liquid		
720a 720b	122 122	Nitrogen rich effluent Nitrogen rich effluent	610 518	K/O drum gas OCM product gas		
720c	122	Nitrogen rich effluent	604	Non-cond. OCM		
720d	504	2 <sup>nd</sup> methane rich effluent	320	prod. gas N <sub>2</sub> /CH <sub>4</sub> gas mixture		
720e 720f	504 502	2 <sup>nd</sup> methane rich effluent 1 <sup>st</sup> methane rich effluent	612 612	Condensate Condensate		
720g	122	Nitrogen rich effluent	612	Condensate		

[0150] The block flow diagram 800 depicted in FIG. 8 shows an optional post-treatment system 802 to which at least a portion of the C<sub>2</sub>-rich effluent 124 is introduced. In at least some instances, the post-treatment system 802 may include any number of unit operations. For example, the post-treatment system 802 may include one or more devices, systems, or processes to provide an ethylene-rich effluent 804. Such an ethylene-rich effluent 804 may be useful in any number of subsequent processes, for example an oligomerization or catalytic polymerization process to produce a liquid gasoline product commonly referred to as polygas.

[0151] In at least some implementations, the post-treatment system 802 includes any number of systems, devices, or processes for reducing the quantity of any acetylene in the  $C_2$ -rich effluent 124. In at least some situations, such reduction may occur by removing as an acetylene-rich effluent 806 at least a portion of any acetylene present in the  $C_2$ -rich effluent 124. In at least some situations, such reduction may occur by converting at least a portion of any acetylene present in the  $C_2$ -rich effluent 124 to one or more preferred chemical species. In at least some implementations, the acetylene concentration in the  $C_2$ -rich effluent 124 can be reduced to less than about 1 part per million by volume

(ppmv); less than about 3 ppmv; less than about 5 ppmv; or less than about 10 ppmv after removal or conversion in the post-treatment system **802**.

[0152] In at least some instances, the C<sub>2</sub>-rich effluent 124 may be further separated the post-treatment system 802. The C<sub>2</sub>-rich effluent **124** may include a number of chemical species that includes a mixture of ethane, ethylene, and  $C_{3+}$ hydrocarbons. In at least some implementations, the ethane, ethylene, and  $C_{3+}$  hydrocarbons may be partially or wholly separated or otherwise isolated in the post-treatment system 802. The separation of the  $C_2$ -rich effluent 124 into a ethane, ethylene, and  $C_{3+}$  can provide at least the ethylene-rich effluent 804, an ethane-rich effluent 808, and a C<sub>3</sub>-rich effluent 810. In at least some implementations, all or a portion of the C<sub>2</sub>-rich effluent **124** may be introduced to one or more systems, devices, or processes in which ethylene may be segregated, removed or otherwise isolated to provide the ethylene-rich effluent 804. In at least some instances, the ethylene-rich effluent 804 may include the overhead product of a distillation or cryogenic distillation process, for example a distillation process including at least one distillation column that is colloquially known within the chemical arts as a "C<sub>2</sub> Splitter" that operates at a reduced temperature and an elevated pressure. In such instances, the ethylene-rich effluent 804 so produced may have an ethylene concentration of about 75 mole percent (mol %) or more; about 80 mol % or more; about 85 mol % or more; about 90 mol % or more; about 95 mol % or more; about 99 mol % or more; or about 99.9 mol % or more.

[0153] In at least some implementations, the mixture of ethane and  $C_{3+}$  hydrocarbons remaining after the removal of at least a portion of the ethylene present in the C<sub>2</sub>-rich effluent 124 may be introduced to one or more systems, devices, or processes in which all or a portion of the ethane may be segregated, removed or otherwise isolated to provide the ethane-rich effluent 808. In at least some instances, the ethane-rich effluent 808 may include at least a portion of the overhead product of a distillation or cryogenic distillation process, for example a distillation process that includes at least one distillation column operating at a reduced temperature and an elevated pressure. In such instances, the ethane-rich effluent 808 so produced may have an ethane concentration of about 75 mole percent (mol %) or more; about 80 mol % or more; about 85 mol % or more; about 90 mol % or more; about 95 mol % or more; about 99 mol % or more; or about 99.9 mol % or more. In such instances, the  $C_{3+}$ -rich effluent 810 may include at least a portion of the bottoms from the ethane separation process. In such instances, the  $C_{3+}$ -rich effluent 810 so produced may have a  $C_{3+}$  hydrocarbon concentration of about 75 mole percent (mol %) or more; about 80 mol % or more; about 85 mol % or more; about 90 mol % or more; about 95 mol % or more; about 99 mol % or more; or about 99.9 mol % or more.

#### Prophetic Example

[0154] Referring to FIG. 2, the following prophetic example illustrates a compositional analysis of an exemplary OCM process in accordance with embodiments disclosed herein with separation of the  $C_2$ -rich effluent 124, the nitrogen-rich effluent 122 and the methane-rich effluent 120.

Ref#	Flow (klb/hr)	C <sub>1</sub> Mol %	N <sub>2</sub> Mol %	O <sub>2</sub> Mol %	H <sub>2</sub> O Mol %	CO Mol %	CO <sub>2</sub> Mol %	C <sub>2</sub> Mol %	C <sub>2</sub> == Mol %
106	36.4	0	78	21	0	0	0	0	0
112	5.8	99	0	0	0	0	0	0	0
110	56.9	48	39	10	0	0	0	0	0
114	56.9	37	39	0	12	1.1	2.4	2	1.8
204	46.9	44	47	0	0	1.3	0	2.4	2.1
120	15.5	97	0.5	0	0	0.5	0	0	0
122	28.6	1	91	0	0	2.2	0	0	0
124	2.8	1	0	0	0	0	0	52	43

[0155] Although described in the context of an oxidative coupling of methane (OCM) process, the disclosed systems and methods can be applied to the separation of a similarly composed C<sub>2</sub>-rich effluent 124 from processes similar to or different from the OCM production process described in detail herein. As an example, another process providing a gaseous effluent similar to the OCM product gas 114 is provided by an oxidative dehydrogenation of ethane to form ethylene using air as the oxygen comprising feed gas.

- 1.-55. (canceled)
- **56**. A process for producing hydrocarbon compounds via oxidative coupling methane (OCM), comprising:
  - (a) directing a feed stream comprising methane and oxygen into an OCM reactor to generate an OCM product gas comprising hydrocarbon compounds with two or more carbon atoms ( $C_{2+}$  compounds);
  - (b) separating at least a portion of said OCM product gas into a first stream and a second stream;
  - (c) expanding at least a portion of said first stream substantially isentropically to produce an expanded first stream; and
  - (d) directing said at least a portion of said first stream expanded in (c) and said second stream into a separations unit to generate a C<sub>2</sub>-rich effluent comprising at least a portion of said C<sub>2+</sub> compounds and an effluent comprising methane.
- 57. The process of claim 56, further comprising, between (a) and (b), condensing at least a portion of said  $C_{2+}$  compounds in said OCM product gas by reducing a temperature of said OCM product gas using one or more heat exchangers.
- **58**. The process of claim **57**, wherein (b) further comprises, directing said at least a portion of said OCM product gas into one or more liquid-gas separators to separate said at least a portion of said OCM product gas into said first stream and said second stream.
- **59**. The process of claim **58**, wherein said first stream comprises at least a portion of said methane, and wherein said second stream comprises at least a portion of condensed  $C_{2+}$  compounds.
- 60. The process of claim 58, wherein (b) further comprises, expanding said at least a portion of said OCM product gas substantially adiabatically in said one or more liquid-gas separators.
- 61. The process of claim 56, further comprising, between (a) and (b), directing said OCM product gas into a carbon dioxide removal treatment unit to reduce a carbon dioxide content of said OCM product gas.

- **62**. The method of claim **61**, wherein said carbon dioxide content of said OCM product gas is reduced to about 20 ppm or less.
- 63. The process of claim 56, further comprising, between (a) and (b), directing said OCM product gas into a treatment unit to reduce a water vapor content of said OCM product gas.
- 64. The process of claim 63, wherein said treatment unit comprises a thermal swing adsorption (TSA) process.
- 65. The process of claim 63, wherein said water vapor content of said OCM product gas is reduced to about 0.01 mole percent or less.
- 66. The process of claim 56, further comprising, directing an additional portion of said first stream and at least a portion of said effluent into an additional separations unit to generate a methane-rich effluent.
- 67. The process of claim 66, wherein said methane-rich effluent has a methane content of at least about 90 mole percent.
- **68**. The process of claim **66**, further comprising, directing at least a portion of said methane-rich effluent into said OCM reactor.
- 69. The process of claim 66, further comprising, adjusting a pressure of said methane-rich effluent to produce one or more methane-rich streams at different pressures.
- 70. The process of claim 69, wherein said one or more methane-rich streams comprise at least (i) a first methane-rich stream at a first pressure between about 5 pounds per square inch gauge (psig) and 30 psig, and (ii) a second methane-rich stream at a second pressure between about 30 psig and about 100 psig.
- 71. The process of claim 66, wherein said separations unit is operated at a first temperature and a first pressure, and wherein said additional separations unit is operated at a second temperature lower than said first temperature and a second pressure lower than said first pressure.
- 72. The process of claim 56, further comprising, (e) directing at least a portion of said  $C_2$ -rich effluent into an acetylene reactor that converts at least a portion of acetylene in said at least a portion of said  $C_2$ -rich effluent to ethylene.
- 73. The process of claim 56, further comprising, (e) separating at least a portion of said  $C_2$ -rich effluent into an ethylene-rich effluent and an ethane-rich effluent.
- 74. The Process of claim 56, wherein said  $C_2$ -rich effluent has an ethylene content of at least about 60 mole percent.
- 75. The Process of claim 56, wherein said  $C_2$ -rich effluent has an ethane content of at least about 60 mole percent.

\* \* \* \*