

TITLE

Process and Apparatus for Producing Oxygen and Nitrogen using Ion Transport Membranes

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to provisional patent application U.S. Ser. No. 61/770,770, titled "Process and Apparatus for Producing Oxygen and Nitrogen using Ion Transport Membranes", filed Feb. 28, 2013, incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under Cooperative Agreement No. DE-FC26-98FT40343 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND

[0003] Air can be separated at high temperatures to produce high-purity oxygen by the use of mixed-conducting multicomponent metallic oxide membranes. These membranes operate by the selective transport of oxygen ions and may be described as ion transport membranes. The mixed-conducting multicomponent metallic oxide material used in ion transport membranes conducts both oxygen ions and electrons, wherein the transported oxygen ions recombine at the product side of the membrane to form oxygen gas.

[0004] The feed gas to ion transport membrane separation systems is an oxygen- and nitrogen-containing gas (for example, air) that is compressed and heated prior its introduction into the membrane system to pressures in the general range of 0.7 MPa (100 psia) to 4.1 MPa (600 psia) and temperatures in the general range of 700°C to 1000°C. A portion of the feed gas is transported through the membrane and is recovered as hot, high-purity oxygen product. The remaining portion of the feed gas is partially depleted of oxygen and still contains a significant amount of heat and pressure energy.

[0005] The hot, pressurized, oxygen-depleted gas may be used in a number of process applications. For example, the significant amount of heat and pressure energy in the gas may be recovered in an expansion turbine to improve the overall economics of oxygen

generation. The ion transport membrane system may be integrated with a gas turbine (combustion turbine) system in a variety of process arrangements to optimize the operation of both systems.

[0006] For example, a synergistic application for ITM systems involves an integrated gasification combined cycle (IGCC) plant, which typically requires large quantities of oxygen for gasification to produce a synthesis gas fuel used to power a gas turbine. In such applications, nitrogen-rich gas streams may also be required for use as a diluent gas and/or dilution gas. A “diluent gas” is used for premixing with a fuel to prevent flashback in the fuel header to the combustor, and/or for direct injection into the primary or secondary combustion zone for NO_x control. “Dilution gas” is introduced into the dilution zone of the combustor and its primary role is to reduce the stream temperature, which has the effect to also lower NO_x formation, but is mainly for liner temperature management and turbine inlet temperature management.

[0007] A typical maximum oxygen content for this diluent nitrogen stream is about 2 mole % for pre-mixing applications, although concentrations up to 16 mole % may be used in some applications with alternative combustion control strategies, for example for NO_x control. As a practical matter, it is advantageous for the ITM system to produce both the oxygen and the nitrogen-rich streams.

[0008] Ion transport membrane (ITM) systems designed to produce tonnage quantities of oxygen use mixed-conducting multicomponent metallic oxide membrane materials that transport of oxygen is based on a difference in the partial pressure of oxygen between the feed and product sides. As an oxygen- and nitrogen-containing feed gas sweeps over a membrane or series of membranes and oxygen passes through the membrane(s), the oxygen content in the feed gas decreases along the flow path. As a result, the maximum theoretical oxygen recovery occurs when the partial pressure of oxygen in the feed falls to point at which it equals the partial pressure of oxygen in the product; an infinite membrane area is required to reach this condition. For example, with pure oxygen product at 103 kPa (15 psia) ($p_{O_2}=103$ kPa (15 psia)) and an oxygen- and nitrogen-containing gas feed at 2068 kPa (300 psia) with 20 mole % oxygen ($p_{O_2}=413$ kPa (60 psia)), maximum theoretical oxygen recovery occurs when only 5 mole % oxygen remains in the oxygen-depleted gas stream. As a practical economic matter, the oxygen-depleted stream would likely contain greater than 5 mole % oxygen in this case. It is difficult to design an ITM system to produce a high-pressure nitrogen product with low oxygen content simply by increasing membrane area because removing a remaining small portion of oxygen from the oxygen-depleted stream can require a very large membrane surface area.

[0009] An alternative way to achieve a low oxygen level (e.g. less than about 2 mole %) is to simply stretch the bounds of total pressure (i.e., increase the ITM feed gas pressure and/or decrease the oxygen product pressure) until the oxygen-depleted stream reaches the desired oxygen content with a reasonable membrane area requirement. However, this strategy leads to significant increases in capital and operating costs for major auxiliary equipment such as, for example, air and/or oxygen compressors requiring higher pressure ratios, larger compressor drive motors, higher pressure ratings for high-temperature heat exchangers, or lower pressure drop allowances for oxygen cooling equipment and piping. Another alternative to achieve an oxygen level of less than about 2 mole % is discussed in EP 0 916 385 to Keskar et al., where a retentate stream from an ion transport separator is sent to a reactively purged ion transport separator. The reactively purged ion transport separator functions as a deoxo unit which separates the residual oxygen by ion transport to the anode side where it reacts with a fuel purge stream to produce a very low partial oxygen pressure and thereby enhance oxygen removal.

[0010] There is a need in the art for improved ion transport membrane processes and systems for the co-production of a high-purity oxygen product and a nitrogen-rich product. There also is a need to maximize the overall efficiency of these processes by recovering energy from any of the hot pressurized effluent gas streams from the ion transport membrane system. These needs are addressed by the embodiments of the invention described below and defined by the claims that follow.

BRIEF SUMMARY

[0011] The present invention relates to an apparatus and a process for producing co-product oxygen and nitrogen streams using ion transport membranes.

[0012] There are several aspects of the apparatus and process as outlined below. The reference numbers and expressions set in parentheses are referring to an example embodiment explained further below with reference to the figures. The reference numbers and expressions are, however, only illustrative and do not limit the aspect to any specific component or feature of the example embodiment. The aspects can be formulated as claims in which the reference numbers and expressions set in parentheses are omitted or replaced by others as appropriate.

[0013] Aspect 1. An apparatus (1) comprising:

a first ion transport membrane assembly (10) having an inlet for introducing a first oxygen- and nitrogen-containing gas (9) comprising oxygen and nitrogen into the first ion transport membrane assembly (10), a first outlet for withdrawing an oxygen-depleted gas (13) from the first ion transport membrane assembly

(10), and a second outlet for withdrawing an oxygen product gas (15) from the first ion transport membrane assembly (10);

a turboexpander (40) having an inlet for introducing a turboexpander feed (85) into the turboexpander (40), at least a portion of the turboexpander feed (85) formed from at least a portion of the oxygen-depleted gas (13) from the first ion transport membrane assembly (10), and an outlet for withdrawing an exhaust gas (45) from the turboexpander, the inlet of the turboexpander (40) in downstream fluid flow communication with the first outlet of the first ion transport membrane assembly (10); and

a second ion transport membrane assembly (20) having an inlet for introducing a second oxygen- and nitrogen-containing gas (7) comprising oxygen and nitrogen into the second ion transport membrane assembly (20), a first outlet for withdrawing a nitrogen product gas (23), and an second outlet for withdrawing an oxygen product gas (25) from the second ion transport membrane assembly (20);

wherein the second ion transport membrane assembly (20) is not in downstream fluid flow communication with the turboexpander (40), and

wherein the turboexpander (40) is not in downstream fluid flow communication with the second ion transport membrane assembly (20).

[0014] Aspect 2. The apparatus of aspect 1 wherein the first ion transport membrane assembly (10) and the second ion transport membrane assembly (20) are contained in a common vessel (30).

[0015] Aspect 3. The apparatus of aspect 2, further comprising a common header operatively disposed to collect the oxygen product gas (15) from the first ion transport membrane assembly (10) and the oxygen product gas (25) from the second ion transport membrane assembly (20) in the common header within the common vessel (30).

[0016] Aspect 4. The apparatus of aspect 1 wherein the first ion transport membrane assembly (10) and the second ion transport membrane assembly (20) are contained in separate vessels.

[0017] Aspect 5. The apparatus of any one of aspects 1 to 4 further comprising an oxygen compressor (100) having an inlet and an outlet, the inlet of the oxygen compressor (100) in downstream fluid flow communication with at least one of the second outlet of the first ion transport membrane assembly (10) for receiving the oxygen product gas (15) from the first ion transport membrane assembly (10), and the second outlet of the second ion transport membrane assembly (20) for receiving the oxygen product gas (25) from the second ion transport membrane assembly (20).

[0018] Aspect 6. The apparatus of any one of aspects 1 to 4 further comprising an oxygen compressor (100) having an inlet and an outlet, the inlet of the oxygen compressor in downstream fluid flow communication with the second outlet of the first ion transport membrane assembly (10) for receiving the first oxygen product gas (15) from the first ion transport membrane assembly (10), and the second outlet of the second ion transport membrane assembly (20) for receiving the oxygen product gas (25) from the second ion transport membrane assembly (20).

[0019] Aspect 7. The apparatus of any one of aspects 1 to 6 further comprising at least one flow control device (6, 8) adapted to control the flow rate of the first oxygen- and nitrogen-containing gas (9) to the first ion transport membrane assembly (10) and/or the flow rate of the second oxygen- and nitrogen-containing gas (7) to the second ion transport membrane assembly (20).

[0020] Aspect 8. The apparatus of any one of aspects 1 to 7 further comprising a gas turbine combustion engine (50) with a combustor, the combustor having one or more inlets for introducing a fuel and a nitrogen-containing diluent gas, the nitrogen-containing diluent gas formed from at least a portion of the nitrogen product gas (23), and an inlet for introducing an oxygen- and nitrogen-containing gas, the combustor in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly (20) for receiving the nitrogen-containing diluent gas.

[0021] Aspect 9. The apparatus of any one of aspects 1 to 8 further comprising a gas turbine combustion engine (50) with a combustor, the combustor having an inlet for introducing a fuel and an inlet for introducing a nitrogen-containing dilution gas, the nitrogen-containing dilution gas formed from at least a portion of the nitrogen product gas, and an inlet for introducing an oxygen- and nitrogen-containing gas, the combustor in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly (20) for receiving the nitrogen-containing dilution gas.

[0022] Aspect 10. The apparatus of any one of aspects 1 to 9 further comprising:

a combustor (60) having one or more inlets and an outlet, the combustor (60) operatively disposed between the first ion transport membrane and the turboexpander (40), the one or more inlets of the combustor (60) operatively disposed to receive a fuel (61) and at least a portion of the oxygen-depleted gas (13) from the first ion transport membrane assembly (10), the outlet of the combustor (60) in upstream fluid flow communication with the inlet of the turboexpander (40).

[0023] Aspect 11. The apparatus of any one of aspects 1 to 10 further comprising a combustion chamber (90) having one or more inlets and an outlet, the one or more inlets of the combustion chamber (90) operatively disposed to receive a fuel (91) and at least a portion of the nitrogen product gas (23) or gas formed therefrom.

5 **[0024]** Aspect 12. A process for producing co-product oxygen and nitrogen streams, the process comprising:

providing the apparatus of any one of aspects 1 to 11;

10 introducing the first oxygen- and nitrogen-containing gas (9) into the inlet of the first ion transport membrane assembly (10), the first oxygen- and nitrogen-containing gas (9) having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the oxygen-depleted gas (13) from the first outlet of the first ion transport membrane assembly (10), and withdrawing the oxygen product gas (15) from the second outlet of the first ion transport membrane assembly (10);

15 introducing the second oxygen- and nitrogen-containing gas (7) into the inlet of the second ion transport membrane assembly (20), the second oxygen- and nitrogen-containing gas (7) having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the nitrogen product gas having a pressure ranging from 689 kPa to 4136 kPa
20 from the second ion transport membrane assembly (20), and withdrawing the oxygen product gas (25) from the second outlet of the second ion transport membrane assembly (20); and

25 expanding the turboexpander feed (85) formed from the oxygen-depleted gas (13) in the turboexpander (40) to recover shaft work or electrical energy and to provide the exhaust gas(45) from the turboexpander (40).

[0025] Aspect 13. A process for producing co-product oxygen and nitrogen streams using the apparatus of any one of aspects 1 to 11, the process comprising:

30 introducing the first oxygen- and nitrogen-containing gas (9) into the inlet of the first ion transport membrane assembly (10), the first oxygen- and nitrogen-containing gas (9) having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the oxygen-depleted gas (13) from the first outlet of the first ion transport membrane assembly (10), and withdrawing the oxygen product gas from the second outlet of the first ion transport membrane assembly (10);

introducing the second oxygen- and nitrogen-containing gas (7) into the inlet of the second ion transport membrane assembly (20), the second oxygen- and nitrogen-containing gas (7) having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the nitrogen product gas (23) having a pressure ranging from 689 kPa to 4136 kPa from the second ion transport membrane assembly (20), and withdrawing the oxygen product gas (25) from the second outlet of the second ion transport membrane assembly (20); and

expanding the turboexpander feed formed from at least a portion of the oxygen-depleted gas in the turboexpander to recover shaft work or electrical energy and to provide the exhaust gas from the turboexpander.

[0026] Aspect 14. The process of aspect 13 wherein the pressure of the oxygen product gas (15) withdrawn from the first ion transport membrane assembly (10) is regulated to within 20 kPa of the pressure of the oxygen product gas (25) from the second ion transport membrane assembly (20).

[0027] Aspect 15. The process of aspect 13 further comprising:

selecting a molar flow rate of the second oxygen- and nitrogen-containing gas (7);

selecting an operating pressure range for the second oxygen- and nitrogen-containing gas (7);

selecting an operating pressure range for the oxygen product gas (25) from the second ion transport membrane assembly (20);

selecting an operating temperature range for the second ion transport membrane assembly (20); and

wherein the second ion transport membrane assembly (20) comprises a first number of membrane units wherein the first number of membrane units are provided in a number sufficient to provide the nitrogen product gas with an oxygen concentration less than 2 mole % oxygen for the selected molar flow rate of the second oxygen- and nitrogen-containing gas (7), the selected operating pressure range for the second oxygen- and nitrogen-containing gas (7), the selected operating pressure range for the oxygen product gas from the second ion transport membrane assembly (20), the selected operating temperature range for the second ion transport membrane assembly (20).

[0028] Aspect 16. The process of aspect 13 wherein the feed to the second ion transport membrane assembly (20) has a molar flow rate, the second ion transport

membrane assembly (20) comprises a first number of membrane units, wherein the first number of membrane units is sufficient to provide the nitrogen product gas with an oxygen concentration less than 2 mole % oxygen, the process further comprising:

regulating the pressure of the second oxygen- and nitrogen-containing gas (7);

5 regulating a pressure of the oxygen product gas from the second ion transport membrane assembly (20);

regulating a temperature in the second ion transport membrane assembly (20);
and

10 wherein the pressure of the second oxygen- and nitrogen-containing gas (7), the pressure of the oxygen product gas from the second ion transport membrane assembly (20), and the temperature in the second ion transport membrane assembly (20) are regulated to provide the nitrogen product gas with an oxygen concentration less than 2 mole % oxygen for the molar flow rate of the feed to the second ion transport membrane assembly (20).

15 **[0029]** Aspect 17. The process of any one of aspects 13 to 16 further comprising introducing a nitrogen-containing diluent gas into a combustor of a gas turbine combustion engine, the nitrogen-containing diluent gas formed from at least a portion of the nitrogen product gas.

20 **[0030]** Aspect 18. The process of any one of aspects 13 to 17 further comprising introducing a nitrogen-containing dilution gas into a dilution zone of a gas turbine combustion engine (50), the nitrogen-containing dilution gas formed from at least a portion of the nitrogen product gas.

25 **[0031]** Aspect 19. The process of aspect 17 wherein the nitrogen-containing diluent gas is formed by combusting a fuel with the at least a portion of the nitrogen product gas (23) with an amount of fuel sufficient to provide the nitrogen-containing diluent gas with an oxygen concentration less than 2 mole % oxygen.

[0032] Aspect 20. The process of any one of aspects 13 to 19 further comprising combusting a fuel with at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly (10) in forming the turboexpander feed (85).

30 **[0033]** Aspect 21. The process of any one of aspects 13 to 20 further comprising recovering heat from at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly (10) and/or from at least a portion of the exhaust gas from the turboexpander (40).

[0034] Aspect 22. The process of any one of aspects 13 to 21 further comprising combusting a fuel with at least a portion of the nitrogen product gas (23) thereby further depleting the oxygen concentration in the nitrogen product gas (23).

5 [0035] Aspect 23. The process of any one of aspects 13 to 22 further comprising recovering heat from at least a portion of the nitrogen product gas (23).

[0036] Aspect 24. The process of any one of aspects 13 to 23 further comprising passing a nitrogen-rich stream to a purification unit and/or de-oxygenation unit to form a high purity nitrogen product having a nitrogen concentration equal to or greater than 99 mole % nitrogen, the nitrogen-rich stream formed from a gas selected from at least one of
10 a portion or all of the oxygen-depleted gas from the first ion transport membrane assembly (10), a portion of the oxygen-depleted gas from the second ion transport membrane assembly (20), a portion or all of the turboexpander exhaust, and a portion or all of the nitrogen product gas.

BRIEF DESCRIPTION OF THE DRAWINGS

15 [0037] The sole figure is a schematic flow diagram of an embodiment of the present invention.

DETAILED DESCRIPTION

[0038] The present invention relates to a process and apparatus for producing an oxygen product and a nitrogen product. The oxygen product may be used, for example, in
20 a gasifier and the nitrogen product may be used, for example, for NO_x control in a gas turbine combustion engine.

[0039] The following definitions apply to terms used in the description of the embodiments of the invention presented herein.

[0040] The articles "a" and "an" as used herein mean one or more when applied to any
25 feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The
30 adjective "any" means one, some, or all indiscriminately of whatever quantity. The term "and/or" placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity. The term "and/or" placed between the last two entities of a list of 3 or more entities means at least one of the entities in the list.

[0041] The phrase “at least a portion” means “a portion or all.” The at least a portion of a stream may have the same composition as the stream from which it is derived. The at least a portion of a stream may include specific components of the stream from which it is derived.

5 **[0042]** As used herein a “divided portion” of a stream is a portion having the same chemical composition as the stream from which it was taken.

[0043] As used herein, “plurality” means two or more.

[0044] As used herein, “in fluid flow communication” means operatively connected by one or more conduits, manifolds, valves and the like, for transfer of fluid. A conduit is any
10 pipe, tube, passageway or the like, through which a fluid may be conveyed. An intermediate device, such as a pump, compressor, heat exchanger, combustor, or vessel, may be present between a first device in fluid flow communication with a second device unless explicitly stated otherwise.

[0045] “Downstream” and “upstream” refer to the intended flow direction of the process
15 fluid transferred. If the intended flow direction of the process fluid is from the first device to the second device, the second device is in downstream fluid flow communication with the first device.

[0046] An ion transport membrane layer is an active layer of ceramic membrane material comprising mixed metal oxides capable of transporting or permeating oxygen
20 ions at elevated temperatures. The ion transport membrane layer also may transport electrons as well as oxygen ions, and this type of ion transport membrane layer typically is described as a mixed conductor membrane layer. The ion transport membrane layer also may include one or more elemental metals thereby forming a composite membrane.

[0047] The membrane layer, being very thin, is typically supported by a porous layer
25 support structure and/or a ribbed support structure. The support structure is generally made of the same material (i.e. it has the same chemical composition), so as to avoid thermal expansion mismatch. However, the support structure might comprise a different chemical composition than the membrane layer.

[0048] A membrane unit, also called a membrane structure, comprises a feed zone, an
30 oxygen product zone, and a membrane layer disposed between the feed zone and the oxygen product zone. An oxygen- and nitrogen-containing gas comprising oxygen and nitrogen is passed to the feed zone and contacts one side of the membrane layer, oxygen is transported through the membrane layer, and an oxygen-depleted gas is withdrawn from the feed zone. An oxygen gas product, which may contain at least 99.0 vol%
35 oxygen, is withdrawn from the oxygen product zone of the membrane unit. The membrane

unit may have any configuration known in the art. When the membrane unit has a planar configuration, it is typically called a “wafer.”

[0049] A membrane module, sometimes called a “membrane stack,” comprises a plurality of membrane units connected together such that each of the individual feed zones from each of the membrane units form a shared feed zone, and that each of the individual oxygen product zones from each of the membrane units form a shared oxygen product zone. The module may have an outlet from which the oxygen product flows from the shared oxygen product zone. Membrane modules may have any configuration known in the art.

[0050] An “ion transport membrane assembly,” also called an “ion transport membrane system,” comprises one or more membrane modules operatively connected together with a shared feed containment zone, and any components necessary to introduce one or more feed streams to the one or more membrane modules and to withdraw two or more effluent streams formed from the one or more feed streams. The components may comprise containment vessels, flow containment duct(s), insulation, manifolds, etc. as is known in the art. When two or more membrane modules are used, the two or more membrane modules in an ion transport membrane assembly may be arranged in parallel and/or in series with respect to the predominate direction of flow of either the feed or permeate streams.

[0051] Exemplary ion transport membrane layers, membrane units, membrane modules, and ion transport membrane assemblies (systems) are described in U.S. Patents 5,681,373, 7,179,323, and 7,955,423 all of which are wholly incorporated herein by reference.

[0052] With reference to the figure, the apparatus 1 comprises a plurality of ion transport membrane assemblies including a first ion transport membrane assembly 10, and a second ion transport membrane assembly 20. The first ion transport membrane assembly and the second ion transport membrane assembly may be contained in a common vessel 30. While the first ion transport membrane assembly and the second ion transport membrane assembly may be contained in a common vessel 30, the feed containment zones of the first ion transport membrane assembly and the second ion transport membrane assembly may be separated by a dividing wall. Alternatively, the first ion transport membrane assembly and the second ion transport membrane assembly may be contained in separate vessels (not shown).

[0053] The first ion transport membrane assembly 10 has an inlet for introducing oxygen- and nitrogen-containing gas 9 comprising oxygen and nitrogen into the first ion

transport membrane assembly 10, a first outlet for withdrawing oxygen-depleted gas 13 from the first ion transport membrane assembly 10, and a second outlet for withdrawing an oxygen product gas 15 from the first ion transport membrane assembly 10.

[0054] The apparatus also comprises a turboexpander 40 having an inlet for introducing a turboexpander feed 85 into the turboexpander 40, the turboexpander feed 85 formed from at least a portion of the oxygen-depleted gas 13 from the first ion transport membrane assembly, and an outlet for withdrawing an exhaust gas 45 from the turboexpander 40. The inlet of the turboexpander is in downstream fluid flow communication with the first outlet of the first ion transport membrane assembly 10. A conduit is operatively disposed between the first ion transport membrane assembly 10 and turboexpander 40, to provide fluid flow communication between the devices.

[0055] A turboexpander, also referred to as a turbo-expander, hot gas expander, or an expansion turbine, is any device through which a gas at a first, higher pressure is expanded to produce work and the gas at a second, lower pressure. The work produced by the turboexpander may be used to drive a compressor, an electric generator, or other suitable device known in the art. In case the turboexpander is used to drive a compressor, the compressor may compress air for forming one or both of the first oxygen- and nitrogen-containing gas 9 and the second oxygen- and nitrogen-containing gas 7.

[0056] The turboexpander feed 85 is formed from at least a portion of the oxygen-depleted gas 13, meaning that the oxygen-depleted gas 13 is used to form the turboexpander feed. The turboexpander feed 85 may be a divided portion of the oxygen-depleted gas 13, where the turboexpander feed has the same composition as the oxygen-depleted gas withdrawn from the first ion transport membrane assembly 10. Alternatively, the oxygen-depleted gas 13 may be "processed" prior to becoming the turboexpander feed 85.

[0057] For example, the apparatus may further comprise a combustor 60 having one or more inlets and an outlet, the combustor operatively disposed between the first ion transport membrane 10 and the turboexpander 40. At least one inlet of the combustor is in downstream fluid flow communication with the first outlet of the first ion transport membrane assembly 10 and the outlet of the combustor 60 is in upstream fluid flow communication with the inlet of the turboexpander 40. The one or more inlets of the combustor 60 is for introducing a combustor feed comprising the oxygen-depleted gas 13 and a fuel 61. The fuel may be added to the oxygen-depleted gas 13, the fuel combusted in combustor 60, thereby reacting oxygen contained in the oxygen-depleted gas 13, resulting in a decreased oxygen concentration in the oxygen-depleted gas 13. The fuel

may be premixed with the oxygen-depleted gas 13 and/or introduced separately into the combustor 60. Air 65 may also be introduced into the combustor 60 in case the oxygen content from the oxygen-depleted gas 13 is not sufficient to combust a desired amount of fuel 61. The outlet of the combustor is for withdrawing a combustor exhaust gas 63 which
5 is used in forming the turboexpander feed 85. Numerous arrangements for introducing oxygen-depleted gas 13, fuel 61, and/or air 61 into a combustor 60 are possible and may be readily configured by one skilled in the art, including for example direct injection, pre-mixing, staged injection, etc.

[0058] The combustor 60 may be any suitable chamber in which combustion occurs.

10 The combustor 60 may contain a catalyst.

[0059] Other unit operations, such as heat exchange, may also be performed on the oxygen-depleted gas 13 prior to use as turboexpander feed 85. The figure shows optional heat exchanger 70 and an additional optional combustor 80.

[0060] The integrated combination of a combustor and turboexpander is often called a
15 combustion turbine. The oxygen-depleted gas 13 may be used as a primary or secondary oxidant stream in the combination combustor/turboexpander. The oxygen-depleted gas 13 may be used to dilute a primary or secondary oxidant stream which is introduced into the combination combustor/turboexpander.

[0061] The second ion transport membrane assembly 20 has an inlet for introducing a
20 second oxygen- and nitrogen-containing gas 7 comprising oxygen and nitrogen into the second ion transport membrane assembly 20, a first outlet for withdrawing nitrogen product gas 23 from the second ion transport membrane assembly 20, and a second outlet for withdrawing an oxygen product gas 25 from the second ion transport membrane assembly 20.

[0062] The first oxygen- and nitrogen-containing gas 9 and the second oxygen- and
25 nitrogen-containing gas 7 may have the same composition. The first oxygen- and nitrogen-containing gas 9 and the second oxygen- and nitrogen-containing gas 7 may be a first portion and a second portion of oxygen- and nitrogen-containing gas 5 as shown in the figure. The benefit of splitting a common oxygen containing gas 5 to form the first
30 oxygen- and nitrogen-containing gas 9 and the second oxygen- and nitrogen-containing gas 7 is that the plurality of ion transport membrane assemblies can share front-end equipment, such as purifiers, air compressors, and heat exchangers.

[0063] As shown in the figure, the feed 85 to the turboexpander 40 and the feed to the
35 second ion transport membrane assembly 20 are formed from separate portions of the oxygen- and nitrogen-containing gas 5. The second ion transport membrane assembly 20

is not in downstream fluid flow communication with the turboexpander 40 and the turboexpander 40 is not in downstream fluid flow communication with the second ion transport membrane assembly 20.

[0064] The apparatus may further comprise an optional oxygen compressor 100. The oxygen compressor 100 has an inlet and an outlet. The inlet of the oxygen compressor 100 is in downstream fluid flow communication with at least one of the second outlet of the first ion transport membrane assembly 10 for receiving the oxygen product gas 15 from the first ion transport membrane assembly 10, and the second outlet of the second ion transport membrane assembly 20 for receiving the oxygen product gas 25 from the second ion transport membrane assembly 20. The oxygen compressor 100 may be in downstream fluid flow communication with one or all of the second outlet of the first ion transport membrane assembly, and the second outlet of the second ion transport membrane assembly. The oxygen product gas 15 and the oxygen product gas 25 may be collected in separate headers. Alternatively, the oxygen product gas 15 and the oxygen product gas 25 may be collected in a common header and fed to oxygen compressor 100. At least a portion of the common header may be inside a vessel 30 containing both the first ion transport membrane assembly 10 and the second ion transport membrane assembly 20. The oxygen compressor may be a multistage compressor where the oxygen product gas 15 and the oxygen product gas 25 are introduced into different stages of the multistage compressor.

[0065] In alternative embodiments, the apparatus may comprise two or more oxygen compressors. For example, a first oxygen compressor may be used to compress at least a portion of the oxygen product gas 15 from the first ion transport membrane assembly 10, and a second oxygen compressor may be used to compress at least a portion of the oxygen product gas 25 from the second ion transport membrane assembly 20. The oxygen product gas 15 from the first ion transport membrane assembly 10, and the oxygen product gas 25 from the second ion transport membrane assembly 20 may be compressed to the same pressure or they may be compressed to different pressures.

[0066] The figure shows the embodiment where the oxygen product gas 15 from the first ion transport membrane assembly 10 and the oxygen product gas 25 from the second ion transport membrane assembly 20 are passed to a common compressor 100. A conduit is operatively disposed in downstream fluid flow communication with the second outlet of the first ion transport membrane assembly 10 for receiving the oxygen product gas from the first ion transport membrane assembly 10. A conduit is operatively disposed in downstream fluid flow communication with the second outlet of the second ion transport membrane assembly 20 for receiving the oxygen product gas 25 from the second ion

transport membrane assembly 20. As shown in the figure, the oxygen compressor 100 has an inlet in downstream fluid flow communication with the first ion transport membrane assembly and the second ion transport membrane assembly 20 for receiving the oxygen product gas from each of the first ion transport membrane assembly 10 and the second ion transport membrane assembly 20.

[0067] The apparatus may further comprise at least one flow control device 6, 8 adapted to control the flow rate of the first oxygen- and nitrogen-containing gas 9 to the first ion transport membrane assembly 10 and/or the flow rate of the second oxygen- and nitrogen-containing gas 7 to the second ion transport membrane assembly 20. Control of the flow rate to the first ion transport membrane assembly 10 and/or the second ion transport membrane assembly 20 ultimately control the flow rate of the turboexpander feed 85 to the turboexpander 40 and/or the flow rate of the nitrogen product gas 23. One or more flow control devices may be installed in any suitable position in the apparatus to vary the split of the oxygen- and nitrogen-containing gas 5 to the first ion transport membrane assembly 10 and the second ion transport membrane 20.

[0068] Although shown as valves, the flow control device(s) may be any device for controlling flow between the ion transport membrane assemblies, such as valves, restrictive piping connecting the vessels to the feed, restrictive piping within the vessel, porous panels, baffles or the like.

[0069] The apparatus may further comprise a gas turbine combustion engine 50 with a combustor having a combustion zone and a dilution zone downstream of the combustion zone. The combustion zone and/or the dilution zone may be in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly 20 for feeding the nitrogen product gas 23 from the second ion transport membrane assembly into the combustion zone and/or the dilution zone of the gas turbine combustion engine 50. The gas turbine combustion engine may also have an inlet for introducing a fuel 51, an inlet for introducing an oxygen-containing gas 53, and an exhaust for discharging an exhaust gas 57. Gas turbine combustion engines are commercially available (for example, from Siemens, GE, MHI, Astom, and others) and the skilled person can readily select a suitable gas turbine combustion engine.

[0070] The apparatus may optionally further comprise a combustion chamber 90 having one or more inlets and an outlet. At least one inlet of the combustion chamber is in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly 20. Combustion chamber feed comprising the nitrogen product gas 23 and a fuel 91 are introduced into the one or more inlets of the combustion chamber 90.

A nitrogen product gas with a decreased oxygen concentration is withdrawn from the outlet of the combustion chamber 90. The fuel 91 may be premixed with the nitrogen product gas 23 and/or introduced separately into the combustion chamber 90. The fuel 91 may be provided in an amount sufficient to reduce the oxygen concentration in the stream to less than 2 mole % oxygen. Additional air 93 may also be introduced into combustor 90.

[0071] Since the article “a” means one or more, the second ion transport membrane assembly may comprise two (or more) ion transport membrane assemblies in parallel and/or series where the nitrogen product gas 23 is withdrawn from one or more of the ion transport membrane assemblies. For example, the second ion transport membrane assembly may further comprise another ion transport membrane assembly (not shown) having an inlet for introducing the nitrogen-rich gas from the first in a series of the second ion transport membrane assembly into the other of the second ion transport membrane assembly. The other ion transport membrane assembly may then have a first outlet for withdrawing nitrogen product gas 23 having a decreased oxygen concentration, and a second outlet for withdrawing an oxygen product gas from the other ion transport membrane assembly. The nitrogen product gas having a decreased oxygen concentration may be introduced into the gas turbine combustion engine 50. The oxygen product gas may be combined with the oxygen product gas from the first and/or second ion transport membrane assemblies.

[0072] The process will be described with reference to the figure.

[0073] The process comprises introducing a first oxygen- and nitrogen-containing gas 9 having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa (100 psia) to 4136 kPa (600 psia) into the first ion transport membrane assembly 10 and a second oxygen- and nitrogen-containing gas 7 having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa (100 psia) to 4136 kPa (600 psia) into the second ion transport membrane assembly 20. An oxygen- and nitrogen-containing gas is defined as a gas that comprises at least oxygen and at least one other component, for example nitrogen, argon, carbon dioxide, carbon monoxide and/or water. For the present process where a nitrogen product is formed, the oxygen- and nitrogen-containing gas comprises at least oxygen and nitrogen. Any oxygen- and nitrogen-containing gas comprising oxygen and nitrogen and known for use with ion transport membrane assemblies may be used. The oxygen- and nitrogen-containing gas may be, for example, air, oxygen-depleted air, or oxygen-enriched air. The oxygen- and nitrogen-containing gas may be exhaust from a combustor which is operated fuel lean and therefore has oxygen in excess of that required to combust all the fuel.

[0074] The oxygen in the oxygen- and nitrogen-containing gas is transported through one or more membrane units to form an oxygen-depleted gas on the feed side of the one or more membrane units and an oxygen product gas on the product side of the one or more membrane units.

5 **[0075]** The process comprises withdrawing an oxygen-depleted gas 13 from the first ion transport membrane assembly 10, and withdrawing an oxygen product gas 15 from the first ion transport membrane assembly 10 to provide an oxygen product gas 15. The process may be operated so that the oxygen-depleted gas is withdrawn at a pressure ranging from 689 kPa (100 psia) to 4136 kPa (600 psia) and a temperature ranging from
10 700°C to 1000°C. The process may be operated so that the oxygen product gas 15 is withdrawn at a pressure ranging from 20 kPa (3 psia) to 315 kPa (45 psia), prior to any recompression step to the final use pressure.

[0076] The process comprises withdrawing a nitrogen product gas 23 from the second ion transport membrane assembly 20, and withdrawing an oxygen product gas 25 from
15 the second ion transport membrane assembly 20 to provide an oxygen product gas 25. The process may be operated so that the nitrogen product gas is withdrawn at a pressure ranging from 689 kPa (100 psia) to 4136 kPa (600 psia) and a temperature ranging from 700°C to 1000°C. The process may be operated so that the oxygen product gas 25 is withdrawn at a pressure ranging from 20 kPa (3 psia) to 315 kPa (45 psia), prior to any
20 recompression step to the final use pressure.

[0077] The process comprises expanding turboexpander feed 85 in the turboexpander 40 to recover shaft work and/or electrical energy and to provide an exhaust stream 45 from the turboexpander 40. The turboexpander feed is formed from the oxygen-depleted gas 13 from the first ion transport membrane assembly 10. The oxygen-depleted gas 13
25 may optionally undergo additional unit operations as part of forming the turboexpander feed 85 and subsequently expanding in turboexpander 40. For example, the oxygen-depleted gas 13 may be mixed with a fuel 61 and the fuel combusted in an optional combustor 60 thereby decreasing the oxygen concentration in the oxygen-depleted gas 13. The fuel may be premixed with the oxygen-depleted gas 13 prior to introducing the
30 mixture into a combustor 60 and/or introduced separately into the optional combustor 60. Additional air 65 may optionally be introduced into combustor 60. Heat may be recovered in an optional heat exchanger 70. The recovered heat may be used for heating any of the feed streams to an ion transport membrane assembly.

[0078] Exhaust stream 45 may be vented or used as feed to a further heat recovery
35 device. Heat from the exhaust stream 45 may be recovered in optional heat exchanger 48,

which may be a heat recovery steam generator (HRSG). Alternately, The recovered heat may be used for heating any of the feed streams to an ion transport membrane assembly.

[0079] The fuel may be any suitable fuel. Since the article “a” means “one or more,” one or more fuels may be used in the process. The fuel(s) may be gaseous, liquid, and/or solid. Example gaseous fuels include natural gas, synthesis gas (syngas), hydrogen, methane, carbon monoxide, and purge or off-gas from a process containing one or more hydrocarbons. Example liquid fuels include liquefied petroleum gas (LPG), liquefied natural gas (LNG), naphtha, methanol, and liquid hydrocarbons. Example solid fuels include coal and petroleum coke.

[0080] Gaseous fuels are generally preferred. However, pumped liquid or solid fuels may be preferred for combustion at high pressure, although specialized combustion equipment may be required.

[0081] A suitable catalyst may be used in the combustor 60 to promote catalytic combustion of the fuel with the oxygen in the oxygen-depleted gas 13.

[0082] In one or more embodiments, a gaseous fuel (e.g. natural gas, synthesis gas, or hydrogen) is introduced and combusted with oxygen in the oxygen-depleted gas 13 in a first combustor 60 to produce a first intermediate gas having a decreased concentration of oxygen compared to the oxygen-depleted gas 13 when removed from the first ion transport membrane assembly 10. The first intermediate gas will comprise nitrogen and products of combustion. The first intermediate gas is passed to heat exchanger 70 where heat is exchanged by indirect heat transfer between the first intermediate gas and an oxygen- and nitrogen-containing feed gas for an ion transport membrane assembly, thereby cooling the first intermediate gas and heating the oxygen- and nitrogen-containing feed gas. Additional gaseous fuel is introduced and combusted with oxygen contained in the cooled intermediate gas in another combustor to produce a second intermediate gas having a further reduced concentration of oxygen compared to the cooled intermediate gas. At least a portion of the turboexpander feed 85 is formed directly from at least a portion of the second intermediate gas. The turboexpander feed is expanded in the turboexpander 40 to recover shaft work and/or electrical energy and to provide exhaust gas 45 from the turboexpander 40.

[0083] The apparatus may further comprise a combustor 80 having one or more inlets and an outlet, the combustor operatively disposed between the first combustor 60 and the turboexpander 40. At least one inlet of the combustor 80 is then in downstream fluid flow communication with the first combustor 60 and the outlet of the combustor 80 is in upstream fluid flow communication with the inlet of the turboexpander 40. The one or

more inlets of the combustor 80 is for introducing a combustor feed comprising effluent 63 from the combustor 60, a fuel 81 and optionally air 83. The fuel may be added to the effluent 63, the fuel combusted in combustor 80, thereby reacting oxygen contained in the stream, resulting in a decreased oxygen concentration in the stream. The fuel may be
5 premixed with the effluent 63 and/or introduced separately into the combustor 80. The outlet of the combustor is for withdrawing a combustor exhaust gas at least a portion of which is used in forming the turboexpander feed 85. A suitable catalyst may also be used.

[0084] Design and operation of a second combustor 80 may be so as to effect or optimize expansion of the turboexpander feed 85 in the turboexpander 40, for example to
10 improve the energy efficiency of the pressure letdown and recovery of work through the turboexpander. Optionally, additional heat may be recovered from the exhaust gas of the turboexpander.

[0085] The process may be operated, for example, such that the oxygen concentration in the nitrogen product gas 23 is less than 2 mole % oxygen. A nitrogen product gas with
15 less than 2 mole % oxygen may be suitable for use as a diluent gas to control NO_x formation in a gas turbine, also called a combustion turbine.

[0086] The nitrogen product gas 23, or a portion thereof, may undergo any number of additional unit operations, for example prior to use as a diluent gas to control NO_x formation in a gas turbine.

[0087] The process may further comprise combusting a fuel 91 with at least a portion of the nitrogen product gas 23 thereby further depleting the oxygen concentration in the nitrogen product gas. The process may be operated such that the oxygen concentration in the nitrogen product gas is reduced to less than 2 mole % oxygen. A nitrogen product gas with less than 2 mole % oxygen may be suitable for use as a diluent gas to control NO_x
20 formation in a gas turbine, also called a combustion turbine. Combustion of a fuel may be accomplished in a combustion chamber 90 or other combustion device for the introduction, mixing, and combustion of fuel 91 with at least a portion of the nitrogen product gas. Any suitable fuel may be used, for example, the fuels discussed above for
25 combusting with the oxygen-depleted gas 13 from the first ion transport membrane assembly 10. A suitable catalyst may also be used.
30

[0088] The process may further comprise recovering heat from at least a portion of the nitrogen product gas. Heat recovery may be accomplished using a heat exchanger 95. The recovered heat may be used to heat an oxygen- and nitrogen-containing gas fed to any of the ion transport membrane assemblies.

[0089] In one embodiment, a gaseous fuel 91 (e.g. natural gas, synthesis gas, or hydrogen) is introduced and combusted with oxygen in at least a portion of the nitrogen product gas 23 in a combustion chamber 90 to produce a nitrogen-rich combustion product gas. The nitrogen-rich combustion product gas is passed to a heat exchanger 95 where heat is exchanged by indirect heat transfer between the nitrogen-rich combustion product gas and an oxygen- and nitrogen-containing feed for an ion transport membrane assembly, thereby cooling the nitrogen-rich combustion product gas and heating the oxygen- and nitrogen-containing feed.

[0090] Design and operation of optional nitrogen-rich gas combustion chamber(s) may be so as to effect and/or optimize heat recovery in heat exchange unit operation and/or reduce the oxygen content of the portion of nitrogen-rich gas.

[0091] Producing nitrogen with less than 2 mole % oxygen may be facilitated by limiting the second portion of oxygen-depleted gas processed in the second ion transport membrane assembly to only the amount required to produce the desired nitrogen product flow rate. This arrangement will require less membrane area than processing all of the original oxygen- and nitrogen-containing gas down to less than 2 mole % oxygen.

[0092] In certain applications, it may be desirable to produce a nitrogen product gas with higher nitrogen purity and/or with lower oxygen concentration relative to the oxygen-depleted gas (e.g. stream 13 in the figure) or nitrogen product gas (e.g. stream 23 in the figure). Nitrogen product gas with higher nitrogen purity and/or with lower oxygen concentration relative to the oxygen-depleted gas or nitrogen-rich gas may be produced by further processing a portion of gas originating from the oxygen-depleted gas and/or the nitrogen-rich gas. Examples of further processing may include cryogenic purification (e.g. using a cryogenic air separation unit), adsorption processes (e.g. using a nitrogen pressure swing adsorption unit), combustion with a fuel (e.g. using a catalytic combustor), and/or other known purification and/or de-oxygenation processes for the production of high purity nitrogen.

[0093] For example, referring to the figure, a portion of gas originating from nitrogen product gas 23 may be provided to a cryogenic air separation unit designed to produce a nitrogen product gas containing 99.9% (or greater) nitrogen. In another example, again referring to the figure, a portion of gas originating from oxygen-depleted gas 13 may be provided to a nitrogen pressure swing adsorption unit designed to produce a nitrogen product gas containing 99.9% (or greater) nitrogen. Nitrogen product gas containing 99.9% (or greater) nitrogen may be used, for example, as a stripping gas in a Selexol™

acid gas removal system in an integrated gasification combined cycle (IGCC) power generation facility.

[0094] From mass balances of the various species in the streams, the skilled person may determine flow rates and compositions of the various streams entering and leaving the first ion transport membrane assembly 10 and the second ion transport membrane assembly 20.

[0095] Once the flow rates and compositions of oxygen- and nitrogen-containing gas fed to each ion transport membrane assembly are known, as well as the individual oxygen product flow rates from each ion transport membrane assembly, one skilled in the art can determine the required membrane surface area, or required number of membrane units or modules. Models may be used to predict oxygen flux per unit area of membrane at a given set of process conditions. Suitable models are available in the literature.

[0096] In general, oxygen production from a membrane assembly can be increased by increasing the membrane surface area (e.g. adding membrane units) or increasing the oxygen flux through the membrane units in the assembly. The oxygen flux through the membranes in the first assembly may be increased by increasing the pressure of the oxygen- and nitrogen-containing feed gas, and/or decreasing the oxygen product pressure, and/or increasing the temperature of the membrane units in the assembly. Similarly, the pressures and/or temperatures may be regulated to increase or decrease the oxygen flux through the membrane units in the second ion transport membrane assembly as desired.

[0097] The process may further comprise selecting a molar flow rate for the second oxygen- and nitrogen-containing gas, and an operating pressure range for the second oxygen- and nitrogen-containing gas 7 and the oxygen product gas 25 from the second ion transport membrane assembly 20. The process may also comprise selecting an operating temperature range of the second ion transport membrane assembly. Each of the ion transport membrane assemblies comprise a number of membrane units, and a sufficient number of membrane units may be provided in each of the ion transport membrane assemblies to provide the nitrogen product gas with an oxygen concentration less than 2 mole % oxygen for the selected pressure ranges and temperature ranges.

[0098] The second oxygen- and nitrogen-containing gas 7 to the second ion transport membrane assembly 20 will have a molar flow rate and the operation of the process to provide less than 2 mole % oxygen in the nitrogen product gas may depend on the molar flow rate of the feed 7. Production of a nitrogen product gas with less than 2 mole % oxygen will also depend on the number of membrane units (i.e. membrane surface area)

in the second ion transport membrane assembly 20. The process may comprise providing a sufficient number of membrane units in the second ion transport membrane assembly 20 to provide the nitrogen product gas with an oxygen concentration less than 2 mole % oxygen. One skilled in the art can determine the number of membrane units sufficient or
5 required to provide a nitrogen product gas with less than 2 mole % oxygen without undue experimentation.

[0099] To provide nitrogen product gas with less than 2 mole % oxygen for the molar flow rate of second oxygen- and nitrogen-containing gas 7, the process may further comprise one or more of regulating or adjusting the pressure of the second oxygen- and
10 nitrogen-containing gas 7, regulating or adjusting the pressure of the oxygen product gas 25 from the second ion transport membrane assembly 20, and regulating or adjusting a temperature in the second ion transport membrane assembly.

[0100] Increasing the pressure of the oxygen- and nitrogen-containing gas increases the oxygen flux through the membranes in the second ion transport membrane assembly and
15 thereby decreases the oxygen concentration in the oxygen-depleted gas, which will in turn decrease the oxygen concentration in the nitrogen product gas. Decreasing the pressure of the oxygen- and nitrogen-containing gas decreases the oxygen flux through the membranes in the second ion transport membrane assembly and thereby increases the oxygen concentration in the oxygen-depleted gas, which will in turn increase the oxygen
20 concentration in the nitrogen product gas. The pressure of the oxygen- and nitrogen-containing gas may be increased or decreased by regulating or adjusting the discharge pressure of a compressor.

[0101] Decreasing the pressure of the second oxygen product gas increases the oxygen flux through the membranes in the second ion transport membrane assembly and thereby
25 decreases the oxygen concentration in the oxygen-depleted gas, which will in turn decrease the oxygen concentration in the nitrogen product gas. Increasing the pressure of the oxygen product gas decreases the oxygen flux through the membranes in the second ion transport membrane assembly and thereby increases the oxygen concentration in the oxygen-depleted gas, which will in turn increase the oxygen concentration in the nitrogen
30 product gas. The pressure of the oxygen product gas may be increased or decreased by regulating or adjusting the suction pressure of oxygen compression equipment connected to the second ion transport membrane assembly, or by regulating or adjusting a backpressure control valve.

[0102] Increasing the temperature in the second ion transport membrane assembly
35 increases the oxygen flux through the membranes in the second ion transport membrane

assembly and thereby decreases the oxygen concentration in the oxygen-depleted gas, which will in turn decrease the oxygen concentration in the nitrogen product gas 23.

Decreasing the temperature in the second ion transport membrane assembly decreases the oxygen flux through the membranes in the second ion transport membrane assembly and thereby increases the oxygen concentration in the oxygen-depleted gas, which will in turn increase the oxygen concentration in the nitrogen product gas. The temperature in the second ion transport membrane assembly may be increased or decreased by regulating or adjusting the heat input to the oxygen- and nitrogen-containing gas upstream of the second ion transport membrane assembly (e.g., adjusting fuel input to a direct- or indirect-fired heater).

[0103] The pressure of the oxygen product gas from the first ion transport membrane assembly may be regulated or adjusted to within 20 kPa (3 psi) of the pressure of the oxygen product gas from the second ion transport membrane assembly, prior to any recompression step to the final use pressure. In this case, a shared oxygen cooling system and/or shared compression equipment can be used for the entire ion transport membrane system. Regulating or adjusting the pressures of the oxygen product gas from each of the ion transport membrane assemblies to be about the same provides the benefit that a single compression train can be used for all assemblies.

[0104] As discussed above, since the nitrogen product gas may be withdrawn from the second ion transport membrane assembly 20 with less than 2 mole % oxygen, the nitrogen product gas may be suitable for use as diluent gas to control NO_x formation in a gas turbine. The process may further comprise introducing a nitrogen-containing diluent gas 55 into the combustor of the gas turbine 50, also called a combustion turbine. The diluent gas may be introduced together with the fuel 53 (i.e. premixed, not shown) or separately from the fuel 53 as shown in the figure. The nitrogen-containing diluent gas is formed from at least a portion of the nitrogen product gas 23. The gas turbine combustor may have a combustion zone and a dilution zone downstream of the combustion zone. A nitrogen-containing dilution gas 59 may be introduced into the dilution zone of the combustor. The nitrogen-containing diluent gas and/or dilution gas may be introduced into the gas turbine at a pressure from 689 kPa (100 psia) to 4136 kPa (600 psia). The nitrogen product withdrawn from the second ion transport membrane assembly may have sufficient pressure that it may be introduced into the gas turbine without further compression.

[0105] The desired nitrogen product flow rate may determine the split of the oxygen- and nitrogen-containing gas 5 into the first oxygen- and nitrogen-containing gas 9 and the second oxygen- and nitrogen-containing gas 7 so that excess nitrogen product is not

produced unnecessarily, thereby minimizing required membrane surface area originally installed into each of the ion transport membrane assemblies. The feed pressure of the oxygen- and nitrogen-containing gas to the second ion transport membrane assembly may be regulated or adjusted so that nitrogen product gas can be used in the gas turbine or other device without further compression.

[0106] The required membrane surface area of an ion transport membrane assembly is defined as the quantity of membranes, measured in square meters, for example, necessary to transport a desired flow rate of oxygen at a given set of process conditions on the feed and product sides (i.e. temperature, pressure, and oxygen concentration).

[0107] An exemplary embodiment of the present invention is illustrated in the schematic flow diagram of the figure. A hot, pressurized, oxygen- and nitrogen-containing gas 5, typically air, is provided from upstream compression and heating devices (not shown) at a typical pressure between 689 kPa (100 psia) and 4136 kPa (600 psia) and a typical temperature between 700°C and 1000°C. This oxygen- and nitrogen-containing gas 5 is divided into a first oxygen- and nitrogen-containing gas 9 and a second oxygen- and nitrogen-containing gas 7. The first oxygen- and nitrogen-containing gas 9 is introduced into representative ion transport membrane assembly 10 shown as having membrane 11 dividing the assembly into feed side or zone 17 and product side or zone 18. This is a schematic representation to illustrate the process discussed here, and it is not meant to describe the structure of an actual ion transport membrane assembly as defined above.

[0108] High-purity oxygen product gas 15, containing greater than 90 mole % oxygen, and typically greater than 99 mole% oxygen, is withdrawn, and oxygen-depleted gas 13 typically containing 3 to 16 mole % oxygen is withdrawn from the feed side.

[0109] The oxygen-depleted gas 13 is expanded in turboexpander 40 to recover shaft work and/or electrical energy, and a low-pressure (LP) nitrogen-rich exhaust 45 is withdrawn.

[0110] The second oxygen- and nitrogen-containing gas 7 is introduced into representative ion transport membrane assembly 20 shown as having membrane 21 dividing the assembly into feed side or zone 27 and product side or zone 28. This is a schematic representation to illustrate the process discussed here, and it is not meant to describe the structure of an actual ion transport membrane assembly as defined above.

[0111] Additional oxygen product gas 25 containing greater than 90 mole % oxygen, and typically greater than 99 mole% oxygen is withdrawn from the second ion transport membrane assembly 20, and a nitrogen product gas 23 is withdrawn as a high-pressure

(HP) nitrogen product gas 23 typically containing, for example, 1.5 to 5 mole % oxygen. The nitrogen product gas 23 withdrawn may contain less than 2 mole % oxygen.

[0112] The schematic diagrams of the first ion transport membrane assembly 10 and the second ion transport membrane assembly 20 each represent any assembly as defined above. An assembly may comprise one or more modules in series and/or parallel flow configuration. As stated above, exemplary ion transport membranes, membrane units, membrane modules, and membrane assemblies (systems) are described in U.S. Patents 5,681,373, 7,179,323, and 7,955,423 all of which are wholly incorporated herein by reference.

[0113] The high pressure (HP) nitrogen product gas 23 may be utilized as a diluent gas 55 or dilution gas 59 to control nitrogen oxide (NO_x) formation in a gas turbine 50. The combustor of a typical gas turbine system may comprise a combustion zone and a dilution zone downstream of the combustion zone, and the combustion zone may have primary and secondary combustion regions. The combustion zone and dilution zone may be disposed in a liner that in turn is disposed in an outer shell of the combustor system. The nitrogen product gas withdrawn, or any portion of gas derived therefrom, may be introduced at any desired location in the gas turbine combustor to control the formation of nitrogen oxide (NO_x) in the gas turbine. The nitrogen product gas may be preferably produced at a pressure between 1034 kPa (150 psia) and 4136 kPa (600 psia).

[0114] In an embodiment for the utilization of the nitrogen product gas, the ion transport membrane assemblies of the figure may be designed and operated so that the oxygen content of the nitrogen product gases less than 2 mole %. This may be effected by selecting design and operating features such as the total membrane surface area resulting from the number of membrane units used in each of ion transport membrane assemblies 10 and 20, and the operating feed and/or oxygen product pressure and/or temperature of the assemblies.

[0115] The air feed pressure to second ion transport membrane assembly 20 may be chosen so that the nitrogen product from second ion transport membrane assembly 20 can be used at pressure without further compression. For example, the diluent pressure specification for a GE 7FB gas turbine is approximately 2.7 MPa (400 psia). When the pressure drops for the various required unit operations are considered, a desired air feed pressure to first ion transport membrane assembly 100 would be about 3.0 MPa (430 psia). This pressure would provide sufficient driving force to achieve the necessary oxygen transport rate that would yield the desired oxygen content of the nitrogen product,

i.e., less than about 2 mole %, at reasonable oxygen product pressure and membrane area requirement.

[0116] We claim:

CLAIMS

1. An apparatus for producing co-product oxygen and nitrogen streams, the apparatus comprising:

5 a first ion transport membrane assembly having an inlet for introducing a first oxygen- and nitrogen-containing gas comprising oxygen and nitrogen into the first ion transport membrane assembly, a first outlet for withdrawing an oxygen-depleted gas from the first ion transport membrane assembly, and a second outlet for withdrawing an oxygen product gas from the first ion transport membrane assembly;

10 a turboexpander having an inlet for introducing a turboexpander feed into the turboexpander, at least a portion of the turboexpander feed formed from at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly, and an outlet for withdrawing an exhaust gas from the turboexpander, the inlet of the turboexpander in downstream fluid flow
15 communication with the first outlet of the first ion transport membrane assembly; and

a second ion transport membrane assembly having an inlet for introducing a second oxygen- and nitrogen-containing gas comprising oxygen and nitrogen into the second ion transport membrane assembly, a first outlet for withdrawing a
20 nitrogen product gas, and an second outlet for withdrawing an oxygen product gas from the second ion transport membrane assembly;

wherein the second ion transport membrane assembly is not in downstream fluid flow communication with the turboexpander, and

25 wherein the turboexpander is not in downstream fluid flow communication with the second ion transport membrane assembly.

2. The apparatus of claim 1 wherein the first ion transport membrane assembly and the second ion transport membrane assembly are contained in a common vessel.

3. The apparatus of claim 1 wherein the first ion transport membrane assembly and the second ion transport membrane assembly are contained in separate vessels.

30 4. The apparatus of claim 3 further comprising:

a combustor having one or more inlets and an outlet, the combustor operatively disposed between the first ion transport membrane and the turboexpander, the one or more inlets of the combustor operatively disposed to receive at least a portion of the oxygen-depleted gas from the first ion transport

membrane assembly and a fuel, the outlet of the combustor in upstream fluid flow communication with the inlet of the turboexpander;

at least one flow control device adapted to control the flow rate of the first oxygen- and nitrogen-containing gas to the first ion transport membrane assembly and/or the flow rate of the second oxygen- and nitrogen-containing gas to the second ion transport membrane assembly;

a gas turbine combustion engine with a combustor, the combustor having an inlet for introducing a fuel, an inlet for introducing a nitrogen-containing dilution gas, the nitrogen-containing dilution gas formed from at least a portion of the nitrogen product gas, and an inlet for introducing an oxygen- and nitrogen-containing gas, the combustor in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly for receiving the nitrogen-containing dilution gas; and

an oxygen compressor having an inlet and an outlet, the inlet of the oxygen compressor in downstream fluid flow communication with at least one of the second outlet of the first ion transport membrane assembly for receiving the oxygen product gas from the first ion transport membrane assembly, and the second outlet of the second ion transport membrane assembly for receiving the oxygen product gas from the second ion transport membrane assembly.

5. The apparatus of claim 3 further comprising:

a combustor having one or more inlets and an outlet, the combustor operatively disposed between the first ion transport membrane and the turboexpander, the one or more inlets of the combustor operatively disposed to receive at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly and a fuel, the outlet of the combustor in upstream fluid flow communication with the inlet of the turboexpander;

at least one flow control device adapted to control the flow rate of the first oxygen- and nitrogen-containing gas to the first ion transport membrane assembly and/or the flow rate of the second oxygen- and nitrogen-containing gas to the second ion transport membrane assembly;

a combustion chamber having one or more inlets and an outlet, the one or more inlets of the combustion chamber operatively disposed to receive a fuel and at least a portion of a gas formed from the nitrogen product gas for combusting the fuel with oxygen contained in the gas formed from the nitrogen product gas thereby decreasing the oxygen concentration in the gas formed from the nitrogen product gas;

a gas turbine combustion engine with a combustor, the combustor having an inlet for introducing a fuel, an inlet for introducing a nitrogen-containing diluent gas, the nitrogen-containing diluent gas formed from at least a portion of the gas formed from the nitrogen product gas, and an inlet for introducing an oxygen- and nitrogen-containing gas, the combustor in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly for receiving the nitrogen-containing diluent gas; and

an oxygen compressor having an inlet and an outlet, the inlet of the oxygen compressor in downstream fluid flow communication with at least one of the second outlet of the first ion transport membrane assembly for receiving the oxygen product gas from the first ion transport membrane assembly, and the second outlet of the second ion transport membrane assembly for receiving the oxygen product gas from the second ion transport membrane assembly.

6. The apparatus of claim 1 further comprising:

an oxygen compressor having an inlet and an outlet, the inlet of the oxygen compressor in downstream fluid flow communication with at least one of the second outlet of the first ion transport membrane assembly for receiving the oxygen product gas from the first ion transport membrane assembly, and the second outlet of the second ion transport membrane assembly for receiving the oxygen product gas from the second ion transport membrane assembly.

7. The apparatus of claim 1 further comprising:

an oxygen compressor having an inlet and an outlet, the inlet of the oxygen compressor in downstream fluid flow communication with the second outlet of the first ion transport membrane assembly for receiving the first oxygen product gas from the first ion transport membrane assembly, and the second outlet of the second ion transport membrane assembly for receiving the oxygen product gas from the second ion transport membrane assembly.

8. The apparatus of claim 1 further comprising at least one flow control device adapted to control the flow rate of the first oxygen- and nitrogen-containing gas to the first ion transport membrane assembly and/or the flow rate of the second oxygen- and nitrogen-containing gas to the second ion transport membrane assembly.

9. The apparatus of claim 1 further comprising a gas turbine combustion engine with a combustor, the combustor having one or more inlets for introducing a fuel and a nitrogen-containing diluent gas, the nitrogen-containing diluent gas formed from at least a

portion of the nitrogen product gas, and an inlet for introducing an oxygen- and nitrogen-containing gas, the combustor in downstream fluid flow communication with the first outlet of the second ion transport membrane assembly for receiving the nitrogen-containing diluent gas.

5 10. The apparatus of claim 1 further comprising a gas turbine combustion engine with a combustor, the combustor having an inlet for introducing a fuel, an inlet for introducing a nitrogen-containing dilution gas, the nitrogen-containing dilution gas formed from at least a portion of the nitrogen product gas, and an inlet for introducing an oxygen- and nitrogen-
10 of the second ion transport membrane assembly for receiving the nitrogen-containing dilution gas.

11. The apparatus of claim 1 further comprising:

15 a combustor having one or more inlets and an outlet, the combustor operatively disposed between the first ion transport membrane and the turboexpander, the one or more inlets of the combustor operatively disposed to receive at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly and a fuel, the outlet of the combustor in upstream fluid flow communication with the inlet of the turboexpander.

12. The apparatus of claim 1 further comprising:

20 a combustion chamber having one or more inlets and an outlet, the one or more inlets of the combustion chamber operatively disposed to receive a fuel and at least a portion of the nitrogen product gas or gas formed therefrom.

13. A process for producing co-product oxygen and nitrogen streams, the process comprising:

25 providing the apparatus of claim 1;

introducing the first oxygen- and nitrogen-containing gas into the inlet of the first ion transport membrane assembly, the first oxygen- and nitrogen-containing gas having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the oxygen-depleted gas from
30 the first outlet of the first ion transport membrane assembly, and withdrawing the oxygen product gas from the second outlet of the first ion transport membrane assembly;

introducing the second oxygen- and nitrogen-containing gas into the inlet of the second ion transport membrane assembly, the second oxygen- and nitrogen-containing gas having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the nitrogen product gas having a pressure ranging from 689 kPa to 4136 kPa from the second ion transport membrane assembly, and withdrawing the oxygen product gas from the second outlet of the second ion transport membrane assembly; and

expanding the turboexpander feed formed from at least a portion of the oxygen-depleted gas in the turboexpander to recover shaft work and/or electrical energy and to provide the exhaust gas from the turboexpander.

14. A process for producing co-product oxygen and nitrogen streams using the apparatus of claim 1, the process comprising:

introducing the first oxygen- and nitrogen-containing gas into the inlet of the first ion transport membrane assembly, the first oxygen- and nitrogen-containing gas having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the oxygen-depleted gas from the first outlet of the first ion transport membrane assembly, and withdrawing the oxygen product gas from the second outlet of the first ion transport membrane assembly;

introducing the second oxygen- and nitrogen-containing gas into the inlet of the second ion transport membrane assembly, the second oxygen- and nitrogen-containing gas having a temperature ranging from 700°C to 1000°C and a pressure ranging from 689 kPa to 4136 kPa, withdrawing the nitrogen product gas having a pressure ranging from 689 kPa to 4136 kPa from the second ion transport membrane assembly, and withdrawing the oxygen product gas from the second outlet of the second ion transport membrane assembly; and

expanding the turboexpander feed formed from at least a portion of the oxygen-depleted gas in the turboexpander to recover shaft work and/or electrical energy and to provide the exhaust gas from the turboexpander.

15. The process of claim 14 wherein the pressure of the oxygen product gas withdrawn from the first ion transport membrane assembly is regulated to within 20 kPa of the pressure of the oxygen product gas from the second ion transport membrane assembly.

16. The process of claim 14 further comprising:

selecting a molar flow rate of the second oxygen- and nitrogen-containing gas;
selecting an operating pressure range for the second oxygen- and nitrogen-
containing gas;

5 selecting an operating pressure range for the oxygen product gas from the second
ion transport membrane assembly; and

selecting an operating temperature range for the second ion transport membrane
assembly;

10 wherein the second ion transport membrane assembly comprises a first number of
membrane units wherein the first number of membrane units are provided in a
number sufficient to provide the nitrogen product gas with an oxygen
concentration less than 2 mole % oxygen for the selected molar flow rate of
the second oxygen- and nitrogen-containing gas, the selected operating
pressure range for the second oxygen- and nitrogen-containing gas, the
15 selected operating pressure range for the oxygen product gas from the second
ion transport membrane assembly, the selected operating temperature range
for the second ion transport membrane assembly.

17. The process of claim 14 wherein the feed to the second ion transport membrane
assembly has a molar flow rate, the second ion transport membrane assembly comprises
20 a first number of membrane units, wherein the first number of membrane units is sufficient
to provide the nitrogen product gas with an oxygen concentration less than 2 mole %
oxygen, the process further comprising:

regulating the pressure of the second oxygen- and nitrogen-containing gas;

25 regulating a pressure of the oxygen product gas from the second ion transport
membrane assembly; and

regulating a temperature in the second ion transport membrane assembly;

30 wherein the pressure of the second oxygen- and nitrogen-containing gas, the
pressure of the oxygen product gas from the second ion transport membrane
assembly, and the temperature in the second ion transport membrane
assembly are regulated to provide the nitrogen product gas with an oxygen
concentration less than 2 mole % oxygen for the molar flow rate of the feed to
the second ion transport membrane assembly.

18. The process of claim 14 further comprising introducing a nitrogen-containing diluent gas into a combustor of a gas turbine combustion engine, the nitrogen-containing diluent gas formed from at least a portion of the nitrogen product gas.

5 18. The process of claim 14 further comprising introducing a nitrogen-containing dilution gas into a dilution zone of a gas turbine combustion engine, the nitrogen-containing dilution gas formed from at least a portion of the nitrogen product gas.

20. The process of claim 18 wherein the nitrogen-containing diluent gas is formed by combusting a fuel with the at least a portion of the nitrogen product gas with an amount of fuel sufficient to provide the nitrogen-containing diluent gas with an oxygen concentration
10 less than 2 mole % oxygen.

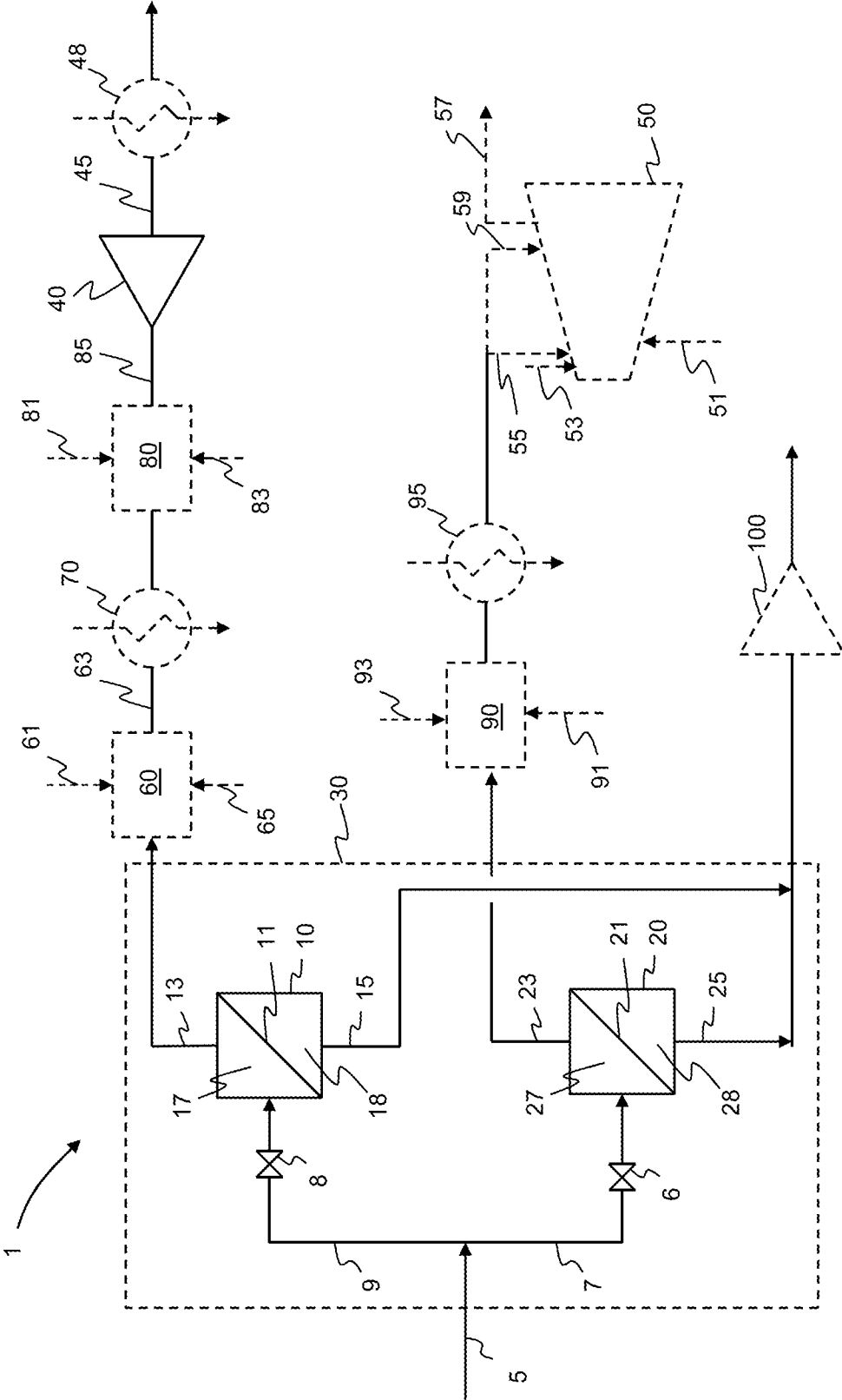
21. The process of claim 14 further comprising combusting a fuel with at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly to provide at least a portion of the turboexpander feed.

22. The process of claim 14 further comprising recovering heat from at least a portion
15 of the oxygen-depleted gas from the first ion transport membrane assembly, a gas formed from at least a portion of the oxygen-depleted gas from the first ion transport membrane assembly, at least a portion of the nitrogen product gas, a gas formed from at least a portion of the nitrogen product gas, and/or from at least a portion of the exhaust gas from the turboexpander.

20 23. The process of claim 14 further comprising combusting a fuel with at least a portion of the nitrogen product gas thereby further depleting the oxygen concentration in the nitrogen product gas.

24. The process of claim 14 further comprising passing a nitrogen-rich stream to a purification unit and/or de-oxygenation unit to form a high purity nitrogen product having a
25 nitrogen concentration equal to or greater than 99 mole % nitrogen, the nitrogen-rich stream formed from a gas selected from at least one of a portion or all of the oxygen-depleted gas from the first ion transport membrane assembly, a portion or all of the turboexpander exhaust, and a portion or all of the nitrogen product gas from the second ion transport membrane assembly.

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FIGURE

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/018838

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C01B13/02 C01B21/04
 ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C01B

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

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

EPO-Internal

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X	EP 0 916 385 A1 (PRAXAIR TECHNOLOGY INC [US]) 19 May 1999 (1999-05-19) cited in the application abstract paragraphs [0033], [0036] - [0037] figure 1	1-24
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Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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