



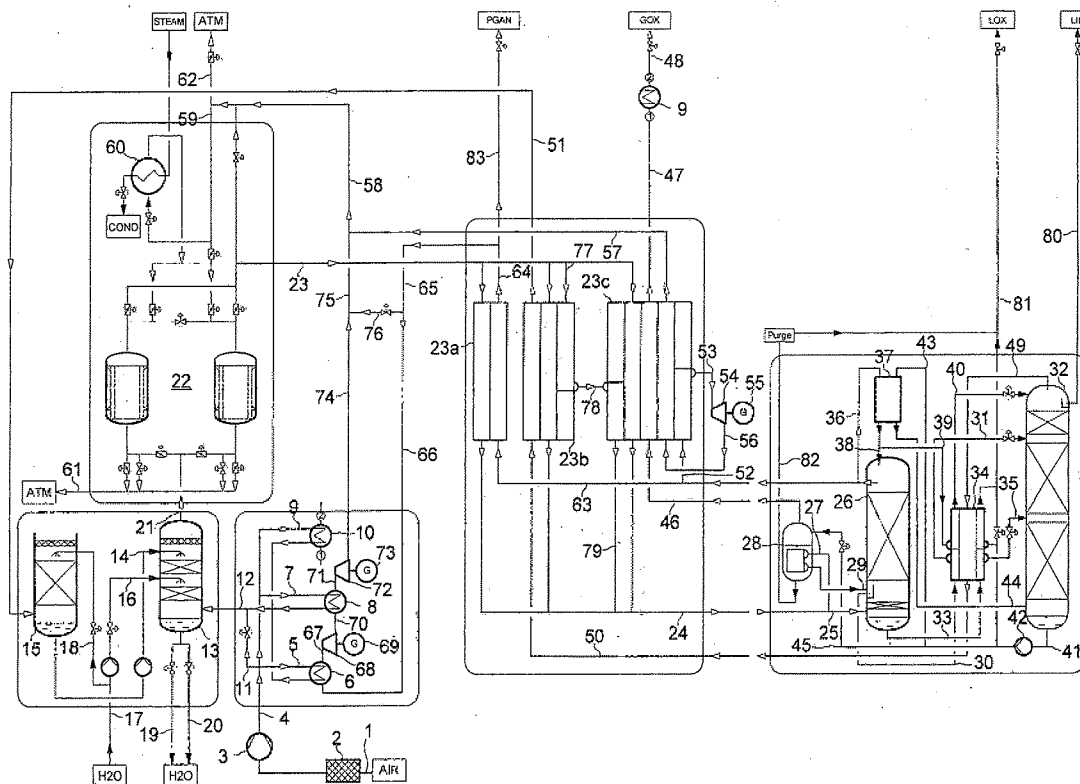
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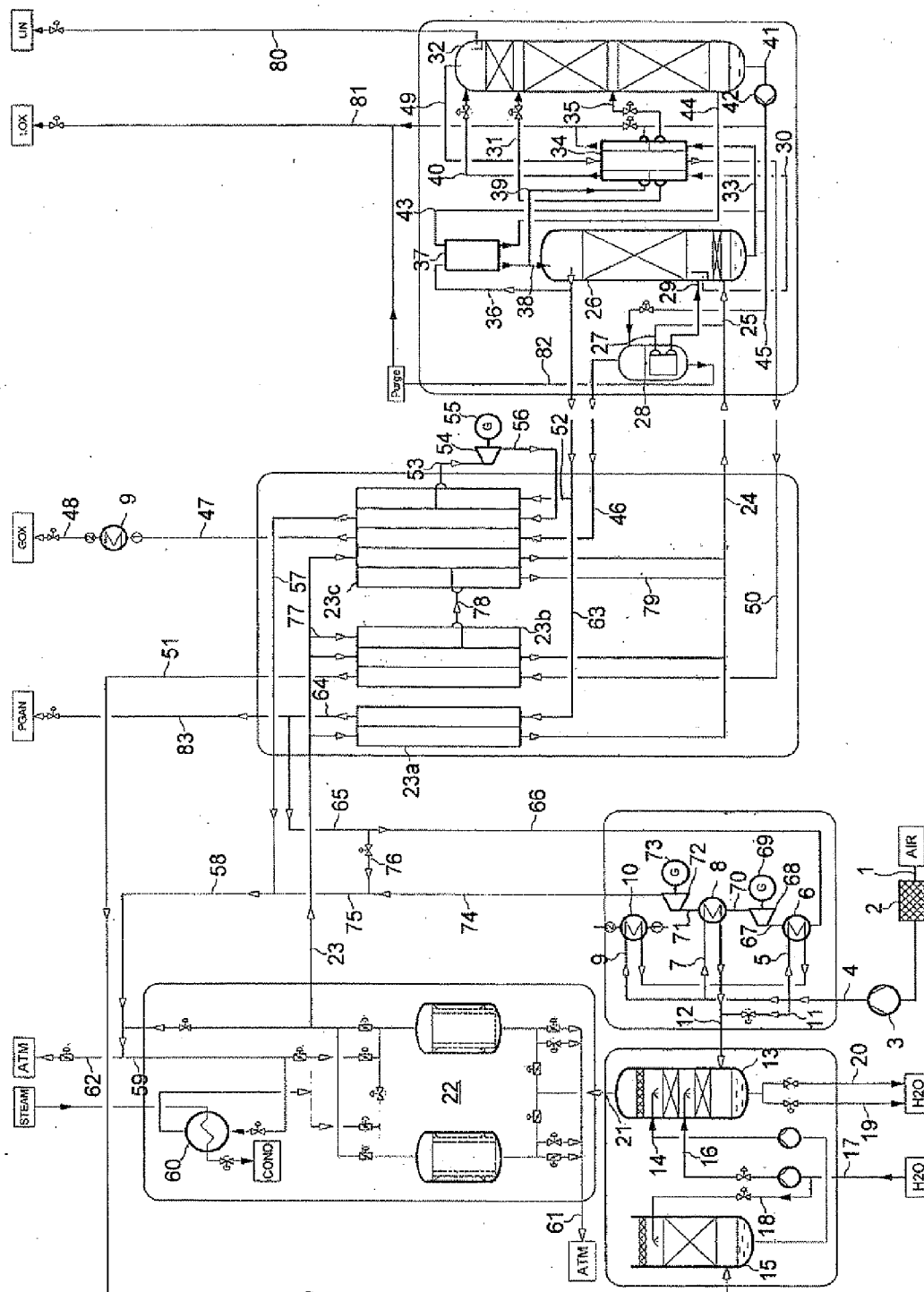
(19) **United States**(12) **Patent Application Publication**
Alekseev(10) **Pub. No.: US 2011/0214453 A1**(43) **Pub. Date: Sep. 8, 2011**(54) **PROCESS AND DEVICE FOR CRYOGENIC AIR FRACTIONATION**(75) Inventor: **Alexander Alekseev**, Munchen (DE)(73) Assignee: **LINDE AKTIENGESELLSCHAFT**, MUNCHEN (DE)(21) Appl. No.: **13/058,723**(22) PCT Filed: **Aug. 11, 2009**(86) PCT No.: **PCT/EP2009/005830**§ 371 (c)(1),
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Publication Classification(51) **Int. Cl.**
F25J 3/04 (2006.01)(52) **U.S. Cl.** 62/644(57) **ABSTRACT**

The process and the device serve for cryogenic air fractionation, in particular for supplying an oxygen-enriched (product) stream to an oxyfuel power plant. The distillation column system for nitrogen/oxygen separation has a high-pressure column (26) and a low-pressure column (32). The high-pressure column (26) and the low-pressure column (32) are thermally coupled via a condenser-evaporator (37). Feed air (1) is compressed in an air compressor (3), cooled at least in a first post-cooler (6) and purified in a purification device (22), cooled in a main heat exchanger (23a, 23b, 23c) and introduced at least in part (25, 29) into the high-pressure column (26). At least one liquid stream (33, 35) is introduced from the high-pressure column (26) into the low-pressure column (32). An oxygen-enriched product stream (41, 45, 46, 47, 48) is taken off from the low-pressure column (32). A first nitrogen stream (63, 64, 65, 66) is withdrawn from the high-pressure column (26) and warmed to a temperature of at least 280 K (6). The warmed first nitrogen stream (67) is work-expanded (72) in a first warm expansion engine (68). The first nitrogen stream (70, 71) which is expanded in the first warm expansion engine (68) is work-expanded in a second warm expansion engine (72).





PROCESS AND DEVICE FOR CRYOGENIC AIR FRACTIONATION

[0001] The invention relates to a process for cryogenic fractionation of air according to the preamble of claim 1.

[0002] The basics of cryogenic fractionation of air in general and specifically the construction of two-column plants are described in the monograph "Tiefemperaturtechnik" [Cryogenic technology] by Hausen/Linde (2nd edition, 1985) and in an article by Latimer in Chemical Engineering Progress (vol. 63, No. 2, 1967, page 35). The thermal coupling between high-pressure column and low-pressure column is generally achieved by a main condenser configured as a condenser-evaporator, in which top gas from the high-pressure column is liquefied against evaporating bottoms liquid from the low-pressure column.

[0003] The feed air for the cryogenic fractionation is compressed in an air compressor and cleaned in a cleaning apparatus before it is cooled to about dew point in a main heat exchanger. The cleaning apparatus preferably works with at least two switchable vessels which comprise an adsorbent, for example a molecular sieve, and have to be regenerated periodically, either by temperature swing (TSA—temperature swing adsorption) or by pressure swing (PSA—pressure swing adsorption). In the course of regeneration, a regeneration gas flows through one of the vessels.

[0004] The warm expansion machine serves to recover compression energy which cannot be utilized in the air fractionation itself. This converts excess energy from the air fractionation to mechanical energy (work). This can be released, for example, to a generator attached to the expansion machine and converted there to electrical energy.

[0005] Processes of the type cited at the outset are known from FR 2690982 A1 and JP 11063811 A.

[0006] It is an object of the invention to improve this process in energetic terms.

[0007] This object is achieved by the characterizing feature of claim 1. In addition to the first warm expansion machine for the first nitrogen stream from the high-pressure column, a second warm expansion machine is used, which is connected in series to the first. Such a two-stage warm expansion has to date been considered to be much too great a level of complexity for the recovery of excess energy. In the context of such warm expansions (frequently referred to as hot gas turbine processes), the use of two-stage or multistage expansions has therefore not been considered to date. In the context of the invention, however, it has been found that, surprisingly, in particular processes, especially those which are used for the oxygen supply of oxyfuel power plants, the energetic advantage exceeds the additional apparatus complexity.

[0008] A "warm expansion machine" is understood here to mean an expansion machine whose inlet temperature is 280 K or more, for example 290 K or more, especially 300 K or more or 320 K or more.

[0009] The inlet temperature of the first warm expansion turbine in the invention is, for example, 330 to 360 K, preferably 340 to 350 K. The first nitrogen stream is expanded there to an intermediate pressure of 2 to 3 bar, preferably 2.1 to 2.5 bar, and then in the second warm expansion turbine from the intermediate pressure to an end pressure of 1.1 to 1.2 bar.

[0010] The high-pressure column has a higher operating pressure than the low-pressure column. Customary values (in

each case at the top of the columns) are 4.5 to 5.2 bar in the high-pressure column, and below 1.4 bar, preferably below 1.25 bar, in the low-pressure column.

[0011] The first nitrogen stream, which is expanded in the warm expansion machines, is withdrawn from the pressure column in gaseous form, for example from the top thereof or from an intermediate site in the upper region of the column. The mechanical energy obtained in the course of expansion of the first nitrogen stream can be utilized directly to drive a compressor; it is preferably converted to electrical energy in generators coupled to each of the expansion machines.

[0012] It is favourable when the warming of the first nitrogen stream is at least partly carried out to the first aftercooler, and the first nitrogen stream is contacted there in indirect heat exchange with the air downstream of the air compressor. This utilizes the waste heat from the air compressor to warm the nitrogen upstream of the work-performing expansion. This increases the energy generated in the expansion. The second nitrogen stream leaves the warm end of the main heat exchanger, for example, at about ambient temperature and is brought further in the first aftercooler to the elevated temperature of 330 to 360 K, preferably 340 to 350 K, and fed at this elevated temperature to the first warm expansion machine. The end temperature, i.e. the exit temperature from the second expansion machine, is then, for example, 283 to 313 K. Alternatively to the warming of the first nitrogen stream, residual heat from another source can be used, for example from an adjacent plant which provides such residual heat.

[0013] The inventive two-stage expansion enables intermediate heating and hence an increased exit temperature from the end stage with the same or even higher energy generation. More particularly, this can save energy when an elevated temperature is required in the further use of the first nitrogen stream—for instance as a regeneration gas.

[0014] More particularly, this involves warming the first nitrogen stream in the first aftercooler and then expanding it in the first expansion machine to an intermediate pressure, and heating the first nitrogen stream expanded to the intermediate pressure in a second downstream compressor and then expanding it in a second expansion machine to an end pressure which is lower than that intermediate pressure. Even if residual heat from another source is used to warm the first nitrogen stream, the transfer of this heat can be performed in two stages arranged upstream of the first and second expansion machines.

[0015] The first and second aftercoolers are preferably connected in parallel on the air side. For intermediate heating, waste heat from the air compressor is thus used once again.

[0016] Preferably, the first nitrogen stream expanded to perform work in the second warm expansion machine is used at least partly as regeneration gas in the cleaning apparatus. Since the offgas from the second expansion machine has a relatively high temperature in the invention, it is possible in this way to save energy which would otherwise be needed for the heating of the regeneration gas.

[0017] It is also favourable when a second nitrogen stream drawn off from the high-pressure column is warmed to an intermediate temperature in the main heat exchanger, and the second nitrogen stream warmed to the intermediate temperature is expanded to perform work in a cold expansion machine and then warmed again in the main heat exchanger. In this way, the compression energy present in the nitrogen from the high-pressure column can also be used to generate process refrigeration.

[0018] The second nitrogen stream expanded to perform work may additionally or alternatively to the first nitrogen stream, be used at least partly as regeneration gas in the cleaning apparatus. It is particularly favourable for operational purposes to use both nitrogen streams as regeneration gas. In the process, two sources of regeneration gas are thus available, one of which is independent of the refrigeration. Thus, coupling of the amount of regeneration gas to the amount of refrigeration generated, which is undesired in operational terms, is eliminated. The amount of regeneration gas and refrigeration generated can be optimized independently of one another. Overall, the process becomes particularly simple and energetically particularly favourable in terms of operation.

[0019] The regeneration gas derived from the first and/or second nitrogen stream, before being introduced into the cleaning apparatus, can be heated in an electrical or steam-operated regeneration gas heater.

[0020] Both the first and the second nitrogen stream are preferably expanded to perform work from the operating pressure of the high-pressure column (minus line losses) to a somewhat superatmospheric pressure which is sufficient to release the streams to the atmosphere after they have flowed through the cleaning apparatus. Use as regeneration gas generally only takes place temporarily when there is a corresponding demand in the cleaning apparatus. At the same time, a portion of the nitrogen expanded to perform work can be released as a gaseous nitrogen product from the cold and/or warm expansion or be released directly to the atmosphere.

[0021] The invention also relates to an apparatus for cryogenic fractionation of air as claimed in claim 8.

[0022] Particularly advantageous configurations are cited in claims 9 to 14.

[0023] The invention further relates to an oxyfuel power plant and to a process for operating an oxyfuel power plant according to claims 15 and 16 respectively.

[0024] The invention and further details of the invention are explained in detail hereinafter with reference to a working example shown schematically in the drawing.

[0025] Atmospheric air 1 is sucked in through a filter 2 by an air compressor 3 and compressed there to a pressure of 4.8 to 5.0 bar. A first part 5 of the compressed feed air 4 is cooled in a first aftercooler 6, a second part in a second aftercooler 8 and a third part 9 in a third aftercooler 10. The air streams from the aftercoolers are subsequently combined, optionally with a fourth part 11, which can be conducted past the aftercoolers via a bypass. The recombined feed air stream 12 is cooled further in a direct contact cooler 13 in direct heat exchange with cooling water (14, 16). The cooling water originates from a fresh water stream 17, of which a first part 16 is introduced directly as cooling water to the direct contact cooler 13, and a second part 18, 14 is cooled beforehand in an evaporation cooler 15. The water obtained at the bottom of the direct contact cooler 13 is drawn off via lines 19 and 20.

[0026] The further-cooled feed air is introduced into a cleaning apparatus 22. This consists in the example of two switchable vessels filled with a molecular sieve as an adsorbent.

[0027] The cleaned air flows toward the warm end of the main heat exchanger, which in the example is formed by three blocks 23a, 23b, 23c connected in parallel on the air side. The feed air 24 cooled to about dew point is for the most part 25 supplied to the high-pressure column immediately above the bottom thereof. A small portion 27 can be condensed in a

secondary condenser 28 and introduced via line 29 in liquid form at an intermediate site in the high-pressure column 16 and/or conducted via line 30/31 directly to the low-pressure column 32.

[0028] The operating pressures of the columns (in each case at the top) in the working example are 4.5 bar in the high-pressure column 26 and 1.2 bar in the low-pressure column 32. The high-pressure column 26 and low-pressure column 32 are thermally coupled via a main condenser 37 configured as a condenser-evaporator. In the example, they are arranged alongside one another and constitute the distillation column system for nitrogen-oxygen separation.

[0029] The oxygen-enriched bottoms liquid 33 from the high-pressure column is cooled in a counter-current subcooler 34 and introduced via line 35 into the low-pressure column 32. A first portion 36 of the gaseous top nitrogen from the high-pressure column 26 is introduced into the liquefying passages of the main condenser 37. A first portion 38 of liquid nitrogen obtained is introduced to the high-pressure column 26, and a second portion 39/40, after passing through the counter-current subcooler 34, to the low-pressure column 32 as return stream. A portion of the nitrogen introduced into the low-pressure column 32 can be released as the liquid product (LIN—liquid nitrogen) via line 80.

[0030] From the bottom of the low-pressure column, oxygen 41 is withdrawn in liquid form with a purity of approx. 40 mol % and brought by means of a pump 42 to a slightly elevated pressure of approx. 4 bar. A first portion 43 of the pumped oxygen is conveyed into the evaporation passages of the main condenser 37 and recycled via line 44 as ascending gas into the low-pressure column 32. A second portion is fed via line 45 as oxygen-enriched product stream into the evaporation space of the secondary condenser 28, virtually completely evaporated, apart from a small purge stream 82. The gaseous oxygen-enriched product stream 46 is warmed to about ambient temperature in the main heat exchanger 23c and heated further (47) in the third aftercooler 9 of the air compressor 3 and finally released via line 48 as the gaseous product (GOX—gaseous oxygen) and especially fed to the combustion chamber of an oxyfuel power plant. A third portion 81 of the oxygen from the pump 42 can be released as liquid product (LOX—liquid oxygen).

[0031] At the top of the low-pressure column 32, gaseous nitrogen 49 is drawn off, warmed in the counter-current subcooler 34, fed via line 50 to the cold end of the main heat exchanger 23b, brought there to about ambient temperature and finally fed as dry gas to the evaporation cooler 15 via line 51.

[0032] A second portion 52 of the gaseous top nitrogen from the high-pressure column 26 is fed as the “second nitrogen stream” to the cold end of the main heat exchanger 23c, removed again via line 53 at an intermediate temperature of 133 K and expanded to 1.2 bar while performing work in a cold expansion machine 54. The expanded second nitrogen stream 56 is passed back again to the cold end of the main heat exchanger 23c, warmed to about ambient temperature and fed via lines 58 and 59 at least partly to the cleaning apparatus 33 as regeneration gas, optionally after further heating in a steam-operated regeneration gas heater 60. Laden regeneration gas 61 is released to the atmosphere.

[0033] A portion of the gas from line 58—or else, if there is temporarily no demand for regeneration gas, the total amount can be blown into the atmosphere via line 62.

[0034] A third portion 63 of the gaseous top nitrogen from the high-pressure column 26 is heated to about ambient temperature in the main heat exchanger 23a as the “first nitrogen stream” and fed at least partly via lines 64, 65 and 66 to the first aftercooler 6 and heated there to about 340 K. The first nitrogen stream 67 heated for the first time is expended to perform work in a first warm expansion machine 68 to an intermediate pressure of about 2.3 bar and a temperature of about 288 K. The first nitrogen stream 70 under the intermediate pressure is heated to about 340 K for a second time in the second aftercooler 8. The first nitrogen stream 71 heated for the second time is expanded to perform work in a second warm expansion machine 72 to an end pressure of about 1.15 bar and a temperature of about 287 K. The first nitrogen stream 74 expanded to the end pressure is mixed via lines 75, 76 with the expanded and warmed second nitrogen stream 57 and likewise used at least partly as regeneration gas for the cleaning apparatus 22. A bypass line 76 can be used to conduct at least a portion of the gas from line 65 past the two warm expansion turbines 69, 72.

[0035] A portion 83 of the pressurized nitrogen 83 warmed in heat exchanger 23a can be released as a gaseous pressurized product (PGAN—pressurized gaseous nitrogen).

[0036] A portion of the feed air 23 can be utilized as a compensation stream 77, 78, 79 between the second block 23b and the third block 23c of the main heat exchanger.

[0037] All expansion machines in the working example are designed as turboexpanders and are slowed by generators 55, 69, 73.

1. A process for cryogenic fractionation of air in a distillation column system for nitrogen-oxygen separation, which has a high-pressure column (26) and a low-pressure column (32), in which

the high-pressure column (26) and the low-pressure column (32) are thermally coupled via a condenser-evaporator (37),

feed air (1) is compressed in an air compressor (3), cooled at least in one first aftercooler (6) and cleaned in a cleaning apparatus (22), cooled in a main heat exchanger (23a, 23b, 23c) and at least partly introduced (25, 29) into the high-pressure column (26),

at least one liquid stream (32, 35) from the high-pressure column (26) is introduced into the low-pressure column (32),

an oxygen-enriched product stream (41, 45, 46, 47, 48) is withdrawn from the low-pressure column (32),

a first nitrogen stream (63, 64, 65, 66) from the high-pressure column (26) is drawn off and warmed (6) to a temperature of at least 280 K, and

the warmed first nitrogen stream (67) is expanded (72) to perform work in a first warm expansion machine (68), characterized in that

the first nitrogen stream (70, 71) expanded in the first warm expansion machine (68) is expanded to perform work in a second warm expansion machine (72).

2. The process as claimed in claim 1, characterized in that the first nitrogen stream is warmed using residual heat, especially the warming of the first nitrogen stream being performed at least partly in the first aftercooler (6) and the first nitrogen stream (66) is brought into indirect heat exchange there with feed air (5) downstream of the air compressor (3).

3. The process as claimed in claim 2, characterized in that the first nitrogen stream (66, 67) is warmed in the first aftercooler (6) upstream of the first warm expansion machine (68),

then expanded in the first expansion machine (68) to an intermediate pressure, and the first nitrogen stream (70) expanded to the intermediate pressure is heated in a second aftercooler (8) and then expanded in the second warm expansion machine (72) to an end pressure which is lower than the intermediate pressure.

4. The process as claimed in claim 3, characterized in that the first and second aftercoolers (6, 8) are connected in parallel on the air side.

5. The process as claimed in claim 1, characterized in that the first nitrogen stream (74) expanded to perform work in the second warm expansion machine (72) is used at least partly as regeneration gas (58, 59) in the cleaning apparatus (22).

6. The process as claimed in claim 1, characterized in that a second nitrogen stream (52) drawn off from the high-pressure column (26) is warmed to an intermediate temperature in the main heat exchanger (23c),

the second nitrogen stream (53) warmed to the intermediate temperature is expanded to perform work in a cold expansion machine (54) and then warmed again in the main heat exchanger (23c).

7. The process as claimed in claim 6, characterized in that the second nitrogen stream (57) expanded to perform work is used at least partly as regeneration gas (58, 59) in the cleaning apparatus (22).

8. An apparatus for cryogenic fractionation of air

comprising a distillation column system for nitrogen-oxygen separation which has a high-pressure column (26) and a low-pressure column (32),

the high-pressure column (26) and the low-pressure column (32) being thermally coupled via a condenser-evaporator (37),

comprising an air compressor (3) for compressing feed air (1), a first aftercooler (6) for cooling compressed feed air (4), a cleaning apparatus (22) for feed air, arranged downstream of the first aftercooler (6), a main heat exchanger (23a, 23b, 23c) for cooling cleaned feed air (23) and a main air line (25) for introducing cooled feed air into the high-pressure column (26),

comprising means for withdrawing at least one liquid stream (33, 35) from the high-pressure column (26) and introduction thereof into the low-pressure column (32),

comprising an oxygen product line for withdrawing an oxygen-enriched product stream (41, 45, 46, 47, 48) from the low-pressure column, comprising a first nitrogen line for withdrawing a first nitrogen stream (63) from the high-pressure column (26),

comprising means (6) for warming the first nitrogen stream (65, 66) to a temperature of at least 280 K and

comprising a first warm expansion machine (68) for work-performing expansion of the warmed first nitrogen stream (67), characterized by a second warm expansion machine (72) for work-performing expansion of the first nitrogen stream (70, 71) expanded in the first warm expansion machine (68).

9. The apparatus as claimed in claim 8, characterized in that the means for warming the second nitrogen stream comprise the first aftercooler (6), which is configured for indirect heat exchange between the first nitrogen stream (66) and compressed feed air (5).

10. The apparatus as claimed in claim 9, characterized in that a second aftercooler (8) is arranged between the first warm expansion machine (68) and the second warm expansion machine (72).

sion machine (72) and is configured for indirect heat exchange between the second nitrogen stream (70) and compressed feed air (7).

11. The apparatus as claimed in claim 10, characterized in that the first and second aftercoolers (6, 8) are connected in parallel on the air side.

12. The apparatus as claimed in claim 8, characterized by means for supplying the first nitrogen stream (74) expanded to perform work in the second warm expansion machine (72) as regeneration gas (58, 59) to the cleaning apparatus (22).

13. The apparatus as claimed in claim 8, characterized by a second nitrogen line for withdrawing a second nitrogen stream (52) from the high-pressure column (26), in which the second nitrogen line leads through the main heat exchanger (23c), leaves the main heat exchanger (23c) at an intermediate site and continues through a cold expansion machine (54) and leads again through the main heat exchanger (23c).

14. The apparatus as claimed in claim 13, characterized by means for supplying the second nitrogen stream (57) expanded to perform work as regeneration gas (58, 59) to the cleaning apparatus.

15. An oxyfuel power plant comprising a combustion chamber and a cryogenic air fractionation plant, in which the cryogenic air fractionation plant is configured as an apparatus as claimed in claim 8 and the oxygen I product line (48) is connected to the combustion chamber.

16. A process for operating an oxyfuel power plant which a combustion chamber and a cryogenic air fractionation plant, in which the cryogenic air fractionation plant is operated according to any of claims 1 to 7 claim 1 and the oxygen-enriched product stream (48) is supplied at least partly to the combustion chamber.

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