ABSTRACT

In a method for separating air by separation at sub-ambient temperature, a first heat pump, using the magnetocaloric effect, exchanges heat between a cold source at sub-ambient temperature and a hot source at sub-ambient temperature, thus providing at least some of the separation energy, and a second heat pump, using the magnetocaloric effect, exchanges heat between a cold source at sub-ambient temperature and a hot source at ambient temperature thus providing at least some of the cold needed to maintain the refrigeration balance of the method, the separation taking place in a single column at a pressure of below 2 bara.
METHOD AND DEVICE FOR SEPARATION AT CRYOGENIC TEMPERATURE

[0001] The present invention relates to a method and to a device for separation at cryogenic temperature. The separation may be a separation by distillation and/or by dephlegmation and/or by absorption. The equipment used for this separation will be referred to as a “column”. Thus, a column may for example be a distillation or absorption column. Reduced to its simplest expression, it may be a phase separator. Otherwise, a column may also be a device in which dephlegmation takes place.

[0002] Magnetic refrigeration relies on the use of magnetic materials that exhibit a magnetocaloric effect. Reversible, this effect is manifested by a variation in their temperature these materials when they are subjected to the application of an external magnetic field. The optimum ranges within which these materials are used lie in the vicinity of their Curie temperature (Tc). This is because the greater the variations in magnetization and, therefore, the changes in magnetic entropy, the greater the changes in their temperature. The magnetocaloric effect is said to be direct when the temperature of the material increases when placed in a magnetic field, and indirect when it cools when placed in a magnetic field. The remainder of the description will be given for the direct case, but it is obvious to a person skilled in the art how to reapply this to the indirect case. There are many thermodynamic cycles based on this principle. A conventional magnetic refrigeration cycle consists i) in magnetizing the material in order to increase its temperature, ii) in cooling the material at a constant magnetic field in order to dissipate the heat, iii) in demagnetizing the material in order to cool it, and iv) in heating the material in a constant (generally zero) magnetic field in order to absorb heat.

[0003] A magnetic refrigeration device employs elements made of magnetocaloric material which generate heat when magnetized and absorb heat when demagnetized. It may employ a magnetocaloric material regenerator to amplify the temperature difference between the “hot source” and the “cold source”: the magnetic refrigeration is then said to be magnetic refrigeration employing active magnetic regeneration.

[0004] It is known from EP-A-2551005 how to use the magnetocaloric effect to supply cold to a method of separation at sub-ambient temperature. U.S. Pat. No. 6,502,404 describes the use of the magnetocaloric effect (in place of the conventional use of an expansion turbine) to supply the cold (needed to provide the refrigeration balance of the method) to a cryogenic method of separating air gases, the separation energy being conventionally supplied by the pressurized air which allows the operation of the vaporizer-condenser of the double column (it being possible for the low-pressure column to be reduced to a simple vaporizer in the case of a nitrogen generator). The separation (distillation) is performed partly under pressure, typically between 5 and 6 bar in the medium-pressure column.

[0005] The present invention tackles the problem of how to perform separation entirely at a very low pressure, the fluid that is to be separated carrying no energy (in the form of pressure) used for the separation and for keeping the process cold. The energy for separation and the energy for keeping cold are supplied by heat pumps, independently of the fluid that is to be separated and the pressure thereof.

[0007] It has long been known how to use one and the same circuit to provide both heat to the reboiler of a distillation column and frigories to the condenser of this same column. U.S. Pat. No. 2,916,888 discloses one example for the distillation of hydrocarbons.

[0008] A heat pump is a thermodynamic device that allows a quantity of heat to be transferred from a medium considered to be the “emitter” and referred to as the “cold source” from which heat is extracted, to a medium considered to be the “receiver” and referred to as the “hot source” to which the heat is supplied, the cold source being at a colder temperature than the hot source.

[0009] The conventional cycle used in the prior art for this type of application is a thermodynamic cycle of compressing-cooling (condensing)-expanding-reheating (vaporizing) a refrigeration fluid.

[0010] FIG. 12 of the document entitled “TECHNIQUES DE L’INGENIEUR—Réfrigération magnétique [Engineering techniques—Magnetic refrigeration] 2005” shows a two-fold improvement in the coefficient of performance of a refrigeration system using a magnetic cycle as compared with the conventional cycle.

[0011] Separating at low pressure, or almost at near-atmospheric pressure, is easier, because of the greater volatility between the components that are to be separated. By combining this effect with the very good performance of heat pumps that employ the magnetocaloric effect, it is possible to arrive at a method with very good separation energy.

[0012] Moreover, separation at low temperature, or even near-atmospheric pressure, allows a simplification in the design and mechanical integrity of the equipment of the separation device, thereby reducing the cost thereof.

[0013] An ambient temperature is the temperature of the ambient air in which the method is situated or, alternatively, a temperature of a cooling water circuit connected with the air temperature.

[0014] A sub-ambient temperature is at least 10° C. below ambient temperature.

[0015] A cryogenic temperature is below −50° C.

[0016] A first subject of the invention provides a method for separating air, by separation at cryogenic temperature, in which:

[0017] a. at least one first heat pump, referred to as the separation heat pump, exchanges heat directly or indirectly between a first cold source at cryogenic temperature and a first hot source at cryogenic temperature thus providing at least some of the separation energy and

[0018] b. at least a second heat pump, referred to as the refrigeration balance heat pump, exchanges heat directly or indirectly between a second cold source at a first cryogenic temperature and a second hot source at a temperature higher than the first temperature, for example at ambient temperature, thus providing at least some of the cold needed to maintain the refrigeration balance of the method, the separation taking place in a single column or a set of columns, the pressure of the single column or of the columns of the set being below 2 bara, preferably below 1.5 bara, preferably at least at a pressure that differs from atmospheric pressure only by the losses in pressure head of the elements that connect the column or columns with the atmosphere, the first cold source and the first hot source being directly or indirectly thermally connected to the single column or to one column of the set, characterized in that the first and second heat pumps use the magnetocaloric effect and in that the second cold source
consists of air (7) intended to be separated in the single column or the set of columns or of a fluid coming from the single column (19) or from a column of the set.

[0019] According to other optional features:

[0020] the first heat pump referred to as the separation heat pump transfers heat directly or indirectly from the column top, preferably by condensing gas of the column, towards the bottom of the column, preferably by vaporizing liquid of the single column;

[0021] the first heat pump referred to as the separation heat pump transfers heat directly or indirectly in a column of the set, preferably by condensing gas in a column of the set, to a column of the set, preferably by vaporization in a column of the set;

[0022] the first and second heat pumps are thermally connected to one another via the single column;

[0023] the second heat pump directly or indirectly at least partially condenses the air before the air is introduced into the single column or into a column of the set;

[0024] the second heat pump directly or indirectly completely condenses part of the air before the completely condensed part of the air is introduced into the single column or into a column of the set, preferably above the supply of the rest of the air;

[0025] by way of end product the method produces at least one gas enriched in a component of the mixture;

[0026] by way of end product the method produces at least one liquid enriched in a component of the mixture;

[0027] the second heat pump, referred to as the refrigeration balance heat pump, directly or indirectly cools or condenses a fluid coming from the single column or from a column of the set in a heat exchanger by an exchange of heat with a heat-transfer fluid of the second heat pump;

[0028] the first heat pump has no heat exchanger in common with the second heat pump;

[0029] at least a fluid that is to be separated and/or that comes from the separation of the column or of a column of the set is brought into direct contact with the magnetocaloric material of one of the first and second heat pumps;

[0030] the exchange of heat is performed at least in part between a fluid that is to be separated and/or that comes from the separation of the column or of a column of the set and a heat-transfer fluid that has been in contact with the magnetocaloric material of one of the first and second heat pumps, through an exchanger;

[0031] the exchange of heat is performed at least in part between a fluid that is to be separated and/or that comes from the separation of the column or of a column of the set and a heat-transfer fluid that has been in contact with the magnetocaloric material of a first and second of the heat pumps, through an intermediate heat-transfer circuit.

[0032] Another subject of the invention provides a device for separating a mixture, for example of air gases, using a method of separation at sub-ambient, or even cryogenic, temperature, comprising a single column or a set of columns in which sub-ambient, or even cryogenic, separation takes place, means for sending a mixture for example of air gases to the column or a column of the set, means for withdrawing at least one fluid enriched in a component of the mixture from the column, or one column of the set, at least a first heat pump, using the magnetocaloric effect, referred to as the separation heat pump, for exchanging heat directly or indirectly between a first cold source at sub-ambient, or even cryogenic, temperature and a first hot source at sub-ambient, or even cryogenic, temperature thus supplying at least part of the separation energy and at least a second heat pump, using the magnetocaloric effect, referred to as the refrigeration balance heat pump, for exchanging heat directly or indirectly between a second cold source at a first sub-ambient, or even cryogenic, temperature and a second hot source at a temperature higher than the first temperature, for example at ambient temperature, thus supplying at least some of the cold needed to maintain the refrigeration balance of the method, the pressure of the single column or of the columns of the set being below 2 bara, preferably below 1.5 bara, so that the column is or the columns are connected to the atmosphere via at least one pipe comprising no expansion means, the first cold source and the first hot source being directly or indirectly thermally connected to the single column or to a column of the set.

[0033] According to other optional subjects:

[0034] the device comprises means for withdrawing a liquid product at the top or bottom of the single column or of a column of the set;

[0035] the device comprises means for withdrawing a gaseous product at the top or bottom of the single column or of a column of the set;

[0036] The invention will be described in greater detail with reference to the figures which illustrate methods according to the invention.

[0037] In FIG. 1, a gaseous air flow 1 is compressed in a compressor 3 and cooled in a cooler 5 to form compressed and cooled air 7. This cooled air 7 is purified in a purification unit 9 to remove water and carbon dioxide and other impurities. The purified air is then cooled in a plate and fin heat exchanger 11. The air cooled in the exchanger 11 is split into two parts 13,15. The part 13 is sent to the middle of a single distillation column in which it separates to form nitrogen-enriched gas at the top of the column 19 and an oxygen-enriched liquid at the bottom of the column 19.

[0038] The part 15 of the air (indirect cold source of the second heat pump) is at least partially condensed in a heat exchanger 17 by exchange of heat with a fluid flow 23 which becomes cool by means of a second heat pump using the magnetocaloric effect 21. A cooling fluid 51 (hot source of the second heat pump), typically ambient air or cooling water, is sent to the second heat pump using the magnetocaloric effect 21. The column comprises a bottom reboiler 33 and a top-end condenser 35. The reboiler (the liquid boiled in the reboiler) is the indirect hot source of the first heat pump) is heated by means of a fluid circuit 37 in connection with a first heat pump using the magnetocaloric effect 31. This first heat pump using the magnetocaloric effect 31 is also used to cool a fluid 39 which cools the top-end condenser 35 (the gas condensed in the condenser is the indirect cold source of the first heat pump). The fluids 37 and 39 may be the same or different. An oxygen-enriched liquid 29 is withdrawn from the bottom of the column 19 and a nitrogen-enriched gas 41 heats up in the exchanger 11 and is then used, at least in part, to regenerate the purification unit 9. An oxygen-enriched gas 25 is withdrawn from the bottom of the column 19, heats up in the exchanger 11 and is compressed by a compressor 27.

[0039] In FIG. 2, unlike in FIG. 1, the fluids 37, 39 are replaced by fluid flows coming from the column 19. The column 19 has neither a top-end condenser nor a bottom reboiler. Part 29A of the bottom liquid (hot source of the first
heat pump) vaporizes in the first heat pump using the magnetocaloric effect and is returned to the column in gaseous form. Part A of the head gas (cold source of the first heat pump) is sent to the first heat pump using the magnetocaloric effect where it condenses. The liquid formed is returned to the top of the column. Likewise, the fluid (cold source of the second heat pump) is sent directly to the second heat pump using the magnetocaloric effect, where it at least partially condenses.

[0040] In FIG. 3, unlike in FIG. 1, the air is not split into two. The entire flow 7 is cooled using a second heat pump using the magnetocaloric effect 21, the heat energy being removed by the heat exchanger 17 and the fluid 23 which cools in a second heat pump using the magnetocaloric effect 21. As a result, the air finds itself partially condensed in the exchanger 17 and is sent to the column 19.

[0041] In FIG. 4, the transfer of heat between the bottom reboiler 33 and the top-end condenser 35 takes place as in FIG. 1, by way of a first heat pump using the magnetocaloric effect 31. By contrast, part 43 of the column head gaseous nitrogen is condensed in the heat exchanger 17 by means of a second heat pump using the magnetocaloric effect 21. The condensed nitrogen is returned to the column so that some of the condensation at the top of the column takes place by means of the second heat pump using the magnetocaloric effect 21.

[0042] Likewise, as can be seen in FIG. 5, part of the oxygen-enriched gas 26 can be cooled and at least partially condensed in a heat exchanger 17 using a fluid circuit 53. The fluid 53 transfers heat to a second heat pump using the magnetocaloric effect 21, which is itself cooled by means of a cooling fluid 51, typically ambient air or cooling water.

[0043] In FIG. 6, the column 19 has a top-end condenser 35 but no bottom reboiler. All of the air intended for the column is cooled by means of a heat exchanger 11, then of a heat exchanger 17 in which it is at least partially condensed, of a fluid 23 and of a second heat pump using the magnetocaloric effect 21. As in FIG. 1, only part of the air may pass into the heat exchanger 17. The nitrogen 41 is heated up and is compressed by a compressor 42. The liquid 29 in the bottom of the column is heated up first of all in the heat exchanger 53, where it is at least partially vaporized, and then in the exchanger 11. A circuit of fluid 55 cools down in the exchanger 53 and collects heat at the first heat pump using the magnetocaloric effect 31. The top-end condenser is cooled as in FIG. 1.

[0044] In FIG. 7, the column has neither a condenser nor a reboiler. All of the air 7 is cooled in the heat exchanger 11, then a heat exchanger 17 in which it is at least partially condensed by means of a second heat pump using the magnetocaloric effect 21, as in FIG. 3. As in FIG. 1, only part of the air may enter the heat exchanger 17. Alternately, all or part of the air may be sent directly to the second heat pump using the magnetocaloric effect 21. The bottom liquid 37 is sent in full to a first heat pump using the magnetocaloric effect 31 where it at least partially vaporizes. The vaporized flow 37A then heats up in the heat exchanger 11 and is used at least partially for regenerating the purification unit 9. The head gas is split into two, part 41 being heated up and compressed and the rest 41A being sent to the first heat pump using the magnetocaloric effect 31 where it is at least partially condensed, forming the flow 41B that is sent to the top of the column.

[0045] The invention is described here in an application to the separation of air at cryogenic temperature. It is obvious that the invention also applies to other separations at sub-ambient temperatures for example to the separation of a mixture containing carbon monoxide and/or hydrogen and/or nitrogen and/or methane.

1-14. (canceled)

15. A method for separating air at a cryogenic temperature, the method comprising the steps of:

a) exchanging heat directly or indirectly between a first cold source at a first cryogenic temperature and a first hot source at a second cryogenic temperature using at least one first heat pump that uses the magnetocaloric effect, thus providing at least some of the separation energy, wherein the at least one first heat pump is referred to as a separation heat pump; and

b) exchanging heat directly or indirectly between a second cold source at a first cryogenic temperature and a second hot source at a temperature higher than the first temperature using at least a second heat pump that uses the magnetocaloric effect, thereby providing at least some of the cold needed to maintain the refrigeration balance of the method, the separation taking place in a single column or a set of columns, the pressure of the single column or of the columns of the set being below 2 bar, wherein the first cold source and the first hot source are directly or indirectly thermally connected to the single column or to one column of the set, wherein the second heat pump is referred to as a refrigeration balance heat pump.

16. The method as claimed in claim 15, in which the first heat pump transfers heat directly or indirectly from the top of the single column or of a column of the set.

17. The method as claimed in claim 16, wherein the heat transfer is done by condensing gas of the column or of a column of the set, towards the bottom of the column or of a column of the set, and by vaporizing liquid of the single column or of a column of the set.

18. The method as claimed in claim 15, wherein the pressure of the single column or of the columns of the set is below 1.5 bar.

19. The method as claimed in claim 15, wherein the single column or of the columns of the set is at a pressure that differs from atmospheric pressure only by the losses in pressure head of elements that connect the column or columns with the atmosphere.

20. The method as claimed in claim 15, in which the first and second heat pumps are thermally connected to one another via the single column.

21. The method as claimed in claim 15, in which the second heat pump directly or indirectly at least partially condenses the air before the air is introduced into the single column or into one of the columns of the set.

22. The method as claimed in claim 15, in which the second heat pump directly or indirectly completely condenses part of the air before the completely condensed part of the air is introduced into the single column or into one of the columns of the set.
23. The method as claimed in claim 22, wherein the completely condensed part of the air is introduced into the single column at a point above the supply of the rest of the air.

24. The method as claimed in claim 15, in which the second heat pump directly or indirectly cools or condenses a fluid coming from the single column or from one of the columns of the set in a heat exchanger thereby allowing an exchange of heat between the fluid and a heat-transfer fluid of the second heat pump.

25. The method as claimed in claim 15, in which at least a fluid that is to be separated and/or that comes from the separation of the column or of one of the columns of the set is brought into direct contact with a magnetocaloric material of one of the first and second heat pumps.

26. The method as claimed in claim 15, in which the exchange of heat is performed at least in part between a fluid that is to be separated and/or that comes from the separation of the column or of a column of the set and a heat-transfer fluid that has been in contact with a magnetocaloric material of one of the first and second heat pumps, through an exchanger.

27. The method as claimed in claim 15, in which the exchange of heat is performed at least in part between a fluid that is to be separated and/or that comes from the separation of the column or of a column of the set and a heat-transfer fluid that has been in contact with a magnetocaloric material of a first and second of the heat pumps, through an intermediate heat-transfer circuit.

28. The method as claimed in claim 15, in which the second heat pump comprises a heat exchanger allowing an exchange of heat between the air that is to be distilled and a heat-transfer fluid of the heat pump.

29. The method as claimed in claim 28, in which the heat exchanger exchanges heat only between the air and the heat-transfer fluid.

30. The method as claimed in claim 28, in which the heat exchanger is used to cool all of the air intended for distillation.

31. The method as claimed in claim 15, in which the first and second heat pumps have no heat exchanger in common.

32. A device for separating air using a method of separation at cryogenic temperature comprising:
   a single column or a set of columns in which cryogenic separation takes place;
   means for sending a mixture of air gases to the column or a column of the set;
   means for withdrawing at least one fluid enriched in a component of the mixture from the column;
   at least a first heat pump, using the magnetocaloric effect, configured to heat directly or indirectly between a cold source at cryogenic temperature and a hot source at cryogenic temperature, thereby supplying at least part of the separation energy, wherein the first heat pump is referred to as the separation heat pump; and
   at least a second heat pump, using the magnetocaloric effect, referred to as the refrigeration balance heat pump, wherein the second heat pump is configured to exchange heat directly or indirectly between a cold source at a first cryogenic temperature consisting of the air intended to be separated in the single column or the set of columns and a hot source at a temperature higher than the first temperature, thus supplying at least a portion of the cold needed to maintain a refrigeration balance when in operation,
   wherein the pressure of the single column or of the columns of the set is below 2 bar, so that the column is or the columns are connected to the atmosphere via at least one pipe that comprises an absence of an expansion means, wherein the first cold source and the first hot source are directly or indirectly thermally connected to the single column or to a column of the set.