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DESCRIPTION

The invention relates to a method and device for recovering cold heat using dry ice at sub-atmospheric pressure. A recovery method is known from US 2003/014879A1.

The term "sub-atmospheric" is intended to be understood to refer in this instance to pressures lower than atmospheric pressure.

Carbon dioxide (CO₂) is used in a number of different applications, ranging from the culinary field to heavy industry.

In the gas industry, for example, methane of fossil origin or biological origin contains CO₂ which it is advantageous to extract, in particular prior to transport of the methane. This is because, before it is transported, the methane gas is liquefied at liquefaction temperatures close to -160°C at atmospheric pressure. Under the same pressure conditions, the CO₂ is solidified at temperatures close to -80°C. Consequently, the liquefied methane is saturated in dry ice, which is problematic for industrial installations.

The CO₂ is therefore logically extracted using different known means, in particular using cleaning techniques. The CO₂ extracted is then discharged into the atmosphere or recycled for other applications.

The present invention relates quite specifically to recycling CO₂ in industrial installations.

The French patent application published under the number FR 2 820 052 (ARMINES) sets out a method and a system which enable the extraction (the capture) of carbon dioxide by means of anti-sublimation at atmospheric pressure, also known as solid condensation. The CO₂ is captured by means of anti-sublimation at a temperature in the order of -80°C at the pressure of 0.89

bar absolute in an anti-sublimation evaporator. A heat transfer fluid is introduced into the anti-sublimation evaporator which, once filled with dry ice, changes into the defrosting phase. The solid CO₂ liquefies and the heat transfer fluid recovers the liquefaction energy. The gross enthalpy variation is 228 kJ/kg. The efficiency of transfer of the exchangers is 90%. The energy recovered by the heat exchange fluid is therefore 205 kJ/kg. The CO₂ further changes from an initial pressure of 0.89 bar absolute in the solid state to a pressure greater than 5.2 bar in the liquid state.

This prior method has major shortcomings. The thermodynamic properties of the CO₂ are not used in an optimum manner. A larger quantity of energy could be recycled using a different method in order to recover a greater cold heat from the dry ice.

To this end, there is proposed, in the first instance, an energy recovery method based on the change of state of the dry ice. This method is implemented using a device comprising:

- an enclosure, containing dry ice at a sub-atmospheric pressure;
- an energy recovering primary circuit which extends through the enclosure and in which a heat exchange fluid circulates.

This method comprises the following steps of:

- passing the heat exchange fluid into the primary circuit, this step causing the dry ice to be warmed and its change of phase into CO₂ and the heat exchange fluid to be cooled;

the method comprising a step of substantially continuously depressurising the enclosure (2) to a sub-atmospheric pressure and a step of transiting the CO₂ extracted from the enclosure (2) into a heat exchanger (9) in which it is warmed again by heat exchange with a heat exchange fluid circulating in a

secondary circuit (14);

- extracting the CO₂ contained in the enclosure, the CO₂ extracted from the enclosure being gaseous.

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This method comprises a step of substantially continuously depressurising the enclosure at a sub-atmospheric pressure.

Various additional features may be provided, alone or in
10 combination:

- the method comprises a step of substantially continuously measuring the pressure in a suction piping by means of a pressure sensor;

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- the method comprises a step of transmitting the pressure measured by the pressure sensor to a central processing unit;

- the method comprises a step of regulating the pressure in
20 the enclosure and in the suction piping, by means of a vacuum pump located at one end of the suction piping;

- the pressure in the enclosure is approximately 0.00055 bar absolute.

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Secondly, there is proposed an energy recovery device configured to implement an energy recovery method as described above, this device comprising:

30 - an enclosure, able to contain dry ice at a sub-atmospheric pressure and at a solidification temperature corresponding to the sub-atmospheric pressure;

- an energy recovery primary circuit which extends through the
35 enclosure and in which a heat exchange fluid circulates;

- a suction piping enabling CO₂ to be extracted from the enclosure.

The suction piping is provided with means able to extract CO₂ and to enable the enclosure to be continuously depressurised to a sub-atmospheric pressure.

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Various additional feature may be provided, alone or in combination:

- 10 - the device comprises a heat exchanger through which the suction piping extends, a secondary circuit also extends through the heat exchanger, the suction piping further comprising a pressure sensor and the means able to extract CO₂ being a vacuum pump;
- 15 - the device comprises a central processing unit, able to process information from the pressure sensor and to regulate the extraction power of the vacuum pump.

20 Other objects and advantages of the invention will be appreciated in the light of the description of an embodiment, set out below with reference to the Figure which is a schematic view of a device for recovering energy from the dry ice.

25 The Figure illustrates a device 1 comprising an enclosure 2 through which a primary energy recovery circuit 3 extends.

The primary circuit 3 comprises a primary pump 4. The primary pump 4 is controlled by a primary motor 5 at a variable speed
30 which is in turn controlled by a primary power variator 6.

A heat transfer fluid circulates in the primary circuit 3. The heat transfer fluid may be liquid or gaseous. If the fluid is gaseous, the primary pump 4 is a compressor.

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The device 1 comprises a suction piping 7 which is provided with a suction pressure sensor 8.

The suction piping 7 extends through a heat exchanger 9 before leaving at an end 10. The end 10 is provided with a vacuum pump 11 which is controlled by a frequency variator 12 which is controlled by a control member 13.

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A secondary heat recovery circuit 14 further extends through the heat exchanger 9. A heat exchange fluid circulates in the secondary circuit 14. The secondary circuit 14 comprises a secondary pump 15. The secondary pump 15 is controlled by a secondary motor 16 at a variable speed which is in turn controlled by a secondary power variator 17.

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The energy recovery method will now be described with reference to the table below:

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Table:

Saturation temperature (°C)	Pressure (bar absolute)	Density (kg/m ³)	Latent sublimation heat (kJ/kg)
-140	0.00055	0.002	593.75
-135	0.00134	0.005	592.0
-130	0.00304	0.011	590.17
-125	0.00646	0.023	588.25
-120	0.01302	0.045	586.24
-115	0.02500	0.083	584.11
-110	0,04598	0.149	581.87
-105	0.08137	0.257	579.50
-100	0.13907	0.427	577.0
-95	0.23033	0.689	574.32
-90	0.37082	1.082	571.49
-85	0.58193	1.660	568.49
-80	0.89239	2.493	565.31

-75	1.3402	3.678	561.92
-70	1.9753	5.341	558.31
-65	2.8626	7.655	554.44
-60	4.0861	10.86	550.25
-57	5.0258	13.35	547.54

The data provided in the table relate to CO₂. This table sets out, starting from the column on the left, the sublimation temperature, the absolute saturation pressure, the density and the latent sublimation heat.

These data are provided by the software Reprop 9 with additional calculations for the latent sublimation heat based on the formulations of the work entitled *Thermodynamic properties in SI* from W. C. Reynolds from the Department of Mechanical Engineering of Stanford University.

In order to illustrate, the energy is decomposed into two parts. One of the parts can be converted into mechanical energy, whilst the other cannot. The part which can be converted into mechanical energy is called exergy. The exergy therefore enables the quality of an energy to be measured.

With regard to CO₂, the lower its temperature is, the higher the exergetic value of the latent heat.

CO₂ in the solid state is referred to as dry ice. At an initial time, the enclosure 2 comprises a specific mass of dry ice. The pressure in the enclosure 2 is sub-atmospheric, that is to say, it is less than the atmospheric pressure which is approximately 1 bar.

This sub-atmospheric pressure is kept constant as a result of the vacuum pump 11. In this embodiment, the pressure in the enclosure is 0.00055 bar absolute or a sublimation temperature of -140°C. The enclosure 2 is covered with efficient insulation in order to reduce the heat exchanges with the

external medium.

The heat transfer fluid circulating in the primary circuit 3 passes through the enclosure 2 and is cooled by means of heat
5 exchange with the dry ice.

The dry ice is heated under the action of the heat transfer fluid and is sublimated instantaneously when the temperature thereof exceeds -140°C at the pressure of 0.00055 bar
10 absolute.

The pressure and the temperature tend naturally to increase under the effect of the sublimation of the dry ice. In order to prevent this, the vacuum pump 11 extracts more gaseous CO_2
15 so that the pressure of 0.00055 bar absolute remains constant so that the sublimation temperature stays at -140°C . This is because, as explained above, the exergetic value of the latent heat becomes higher as the sublimation temperature decreases.

20 The energy recovery is carried out until complete sublimation of the dry ice. After the dry ice has fully disappeared, the enclosure 2 is refilled with dry ice.

The control of the pressure in the enclosure 2 is carried out
25 by measuring the pressure in the suction piping 7 by means of the suction pressure sensor 8.

The value of the pressure in the suction piping 7 is sent continuously to a central processing unit which is not
30 illustrated in the drawings.

When the pressure in the suction piping 7 exceeds the target pressure, in this instance 0.00055 bar absolute, then the central processing unit instructs the vacuum pump 11, via the
35 control member 13 and the frequency variator 12, to extract more gaseous CO_2 so that the target pressure is reached and remains constant in the suction piping 7. The pressures in the enclosure 2 and in the suction piping 7 are substantially

identical.

The gaseous CO₂ leaving the enclosure 2 passes through the heat exchanger 9 and gives off a portion of its sensible heat to the heat transfer fluid circulating in the secondary circuit 14.

The flow rates of the heat transfer fluids in the primary circuit 3 and in the secondary circuit 14 may be adapted so that the heat exchanges with the dry ice for the primary circuit 13 and with the gaseous CO₂ for the secondary circuit 14 are as efficient as possible.

In this manner, a portion of the sensible heat is recovered by the secondary circuit 14. The sensible heat in contrast to the latent heat corresponds to the energy discharged without there being a change of state of the CO₂.

Advantageously, the heat transfer fluid in the secondary circuit 14 and the CO₂ in the suction piping 7 circulate in counter-current.

The heat transfer fluid must be able not to solidify at these cryogenic temperatures close to -140°C. Propane may advantageously be used as a heat transfer fluid for this reason.

The transfer of heat in the heat exchanger 9 is based on large temperature deviations. Typically, this deviation extends from -140°C to 20°C. The sensible heat is approximately 120 kJ/kg.

In the enclosure 2, the latent sublimation heat is approximately 594 kJ/kg, with reference to the table.

The total recoverable heat is therefore approximately 714 kJ/kg. With equipment which enables a heat exchange which is 90% efficient, the total heat effectively recovered is approximately 643 kJ/kg.

The method and device thus described enable a much more efficient recovery of energy from the dry ice, by advantageously using the thermodynamic properties of carbon
5 dioxide.

Patentkrav

1. Fremgangsmåde til genvinding af energi, der stammer fra tilstandsændringen af tør is, hvilken fremgangsmåde iværksættes ved hjælp af en anordning (1), der omfatter:

- et indelukke (2), der indeholder tørisen ved et infra-atmosfærisk tryk;

- et primært energigenvindingskredsløb (3), der går igennem indelukket (2), og i hvilket strømmer et varmeoverføringsmedium;

idet fremgangsmåden omfatter følgende trin:

- passage af varmeoverføringsmediet i det primære kredsløb (3), idet dette trin bevirker en opvarmning af tørisen og ændring af dens tilstand til CO₂ samt afkøling af varmeoverføringsmediet;

- udtagning af det CO₂, der er indeholdt i indelukket (2); idet det CO₂, der udtages fra indelukket (2), er gasformigt; idet fremgangsmåden omfatter

et trin til etablering af tilnærmelsesvis kontinuert undertryk i indelukket (2) ved et infra-atmosfærisk tryk, og et trin til gennemløb af det CO₂, der er udtaget fra indelukket (2), i en varmeveksler (9), i hvilken det opvarmes ved varmeveksling med et varmeoverføringsmedium, der strømmer i et sekundært kredsløb (14).

2. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at fremgangsmåden omfatter et trin til tilnærmelsesvis kontinuert måling af trykket i en sugeledning (7) ved hjælp af en trykføler (8).

3. Fremgangsmåde ifølge krav 2, kendetegnet ved, at fremgangsmåden omfatter et trin til transmission af trykket, der er målt af trykføleren (8), til en centralenhed.

4. Fremgangsmåde ifølge krav 3, kendetegnet ved, at fremgangsmåden omfatter et trin til regulering af trykket i indelukket (2) og sugeledningen (7) ved hjælp af en

vakuumpumpe (11), der er placeret i en ende af sugeslangen (7).

5. Fremgangsmåde ifølge et hvilket som helst af de
5 foregående krav, kendetegnet ved, at det absolute tryk i indelukket (2) ligger på omtrent 0,00055 bar.

6. Energigenvindingsanordning (1), der er udformet til
10 iværksætte en energigenvindingsfremgangsmåde ifølge et af kravene 1 eller 2, hvilken anordning (1) omfatter:

- et indelukke (2), der er egnet til at indeholde tør is ved et infra-atmosfærisk tryk og en størkningstemperatur svarende til det infra-atmosfæriske tryk;

- et primært energigenvindingskredsløb (3), der går igennem
15 indelukket (2), og i hvilket strømmer et varmeoverføringsmedium;

- en sugeledning (7), der gør det muligt at udtage CO₂ fra indelukket (2),

idet sugeledningen (7) er forsynet med midler, som er egnede
20 til at udtage CO₂ og muliggøre etablering af kontinuert undertryk i indelukket (2) ved et infra-atmosfærisk tryk, og ved, at anordningen (1) desuden omfatter et sekundært kredsløb (14) og en varmeveksler (9), som sugeledningen (7) og det sekundære kredsløb (14) går igennem.

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7. Anordning (1) ifølge krav 6 til iværksættelse af fremgangsmåden ifølge et af kravene 3 eller 4, kendetegnet ved, at sugeledningen (7) desuden omfatter en trykføler (8), og midlerne, som er egnede til at udtage CO₂, er en vakuumpumpe
30 (11).

8. Anordning (1) ifølge krav 7 til iværksættelse af fremgangsmåden ifølge et af kravene 5 eller 6, kendetegnet ved, at anordningen (1) omfatter en centralenhed, der er egnet
35 til at behandle de informationer, som stammer fra trykføleren (8), og til at regulere vakuumpumpens (11) udtagningskraft.

