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(54) PROCESS FOR REMOVING CARBON DIOXIDE FROM A GAS STREAM USING DESUBLIMATION

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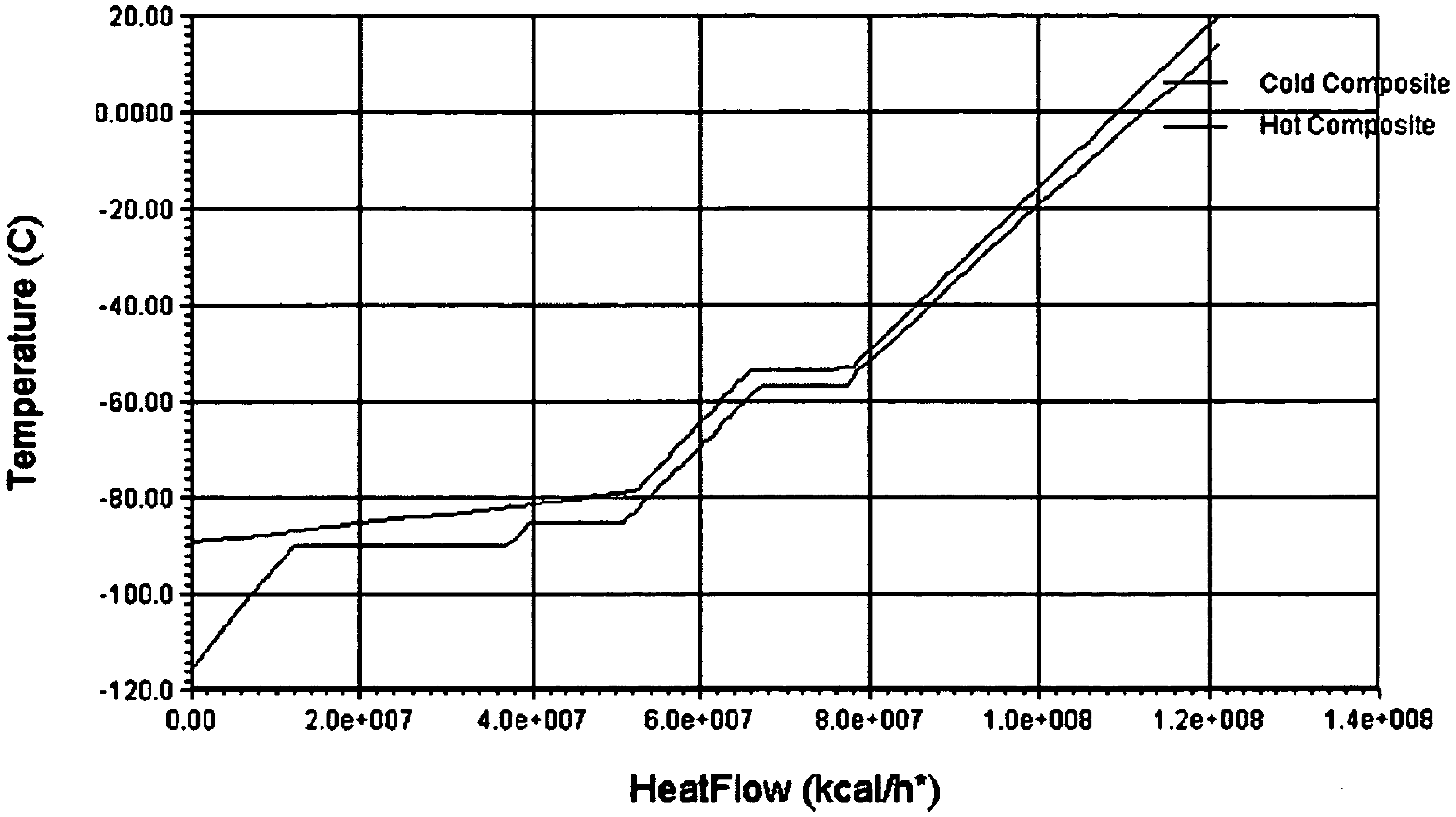
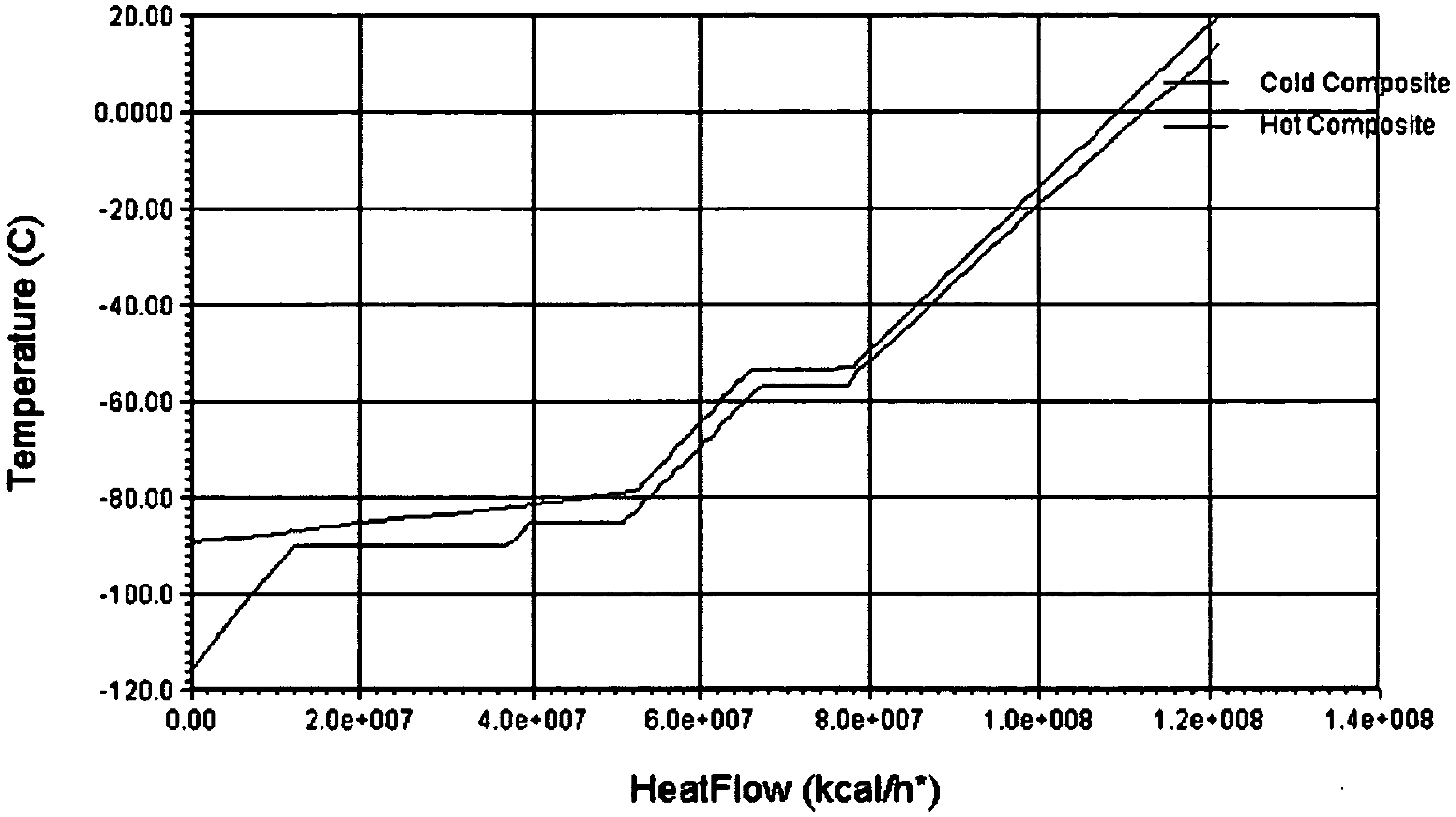
(57) **ABSTRACT**

A process for removing carbon dioxide from a carbon dioxide containing gas stream is obtained through de-sublimation, vaporization, and liquefaction of various carbon dioxide-containing streams with little or no external refrigeration.

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Temperature (C)
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4.0e+007
6.0e+007
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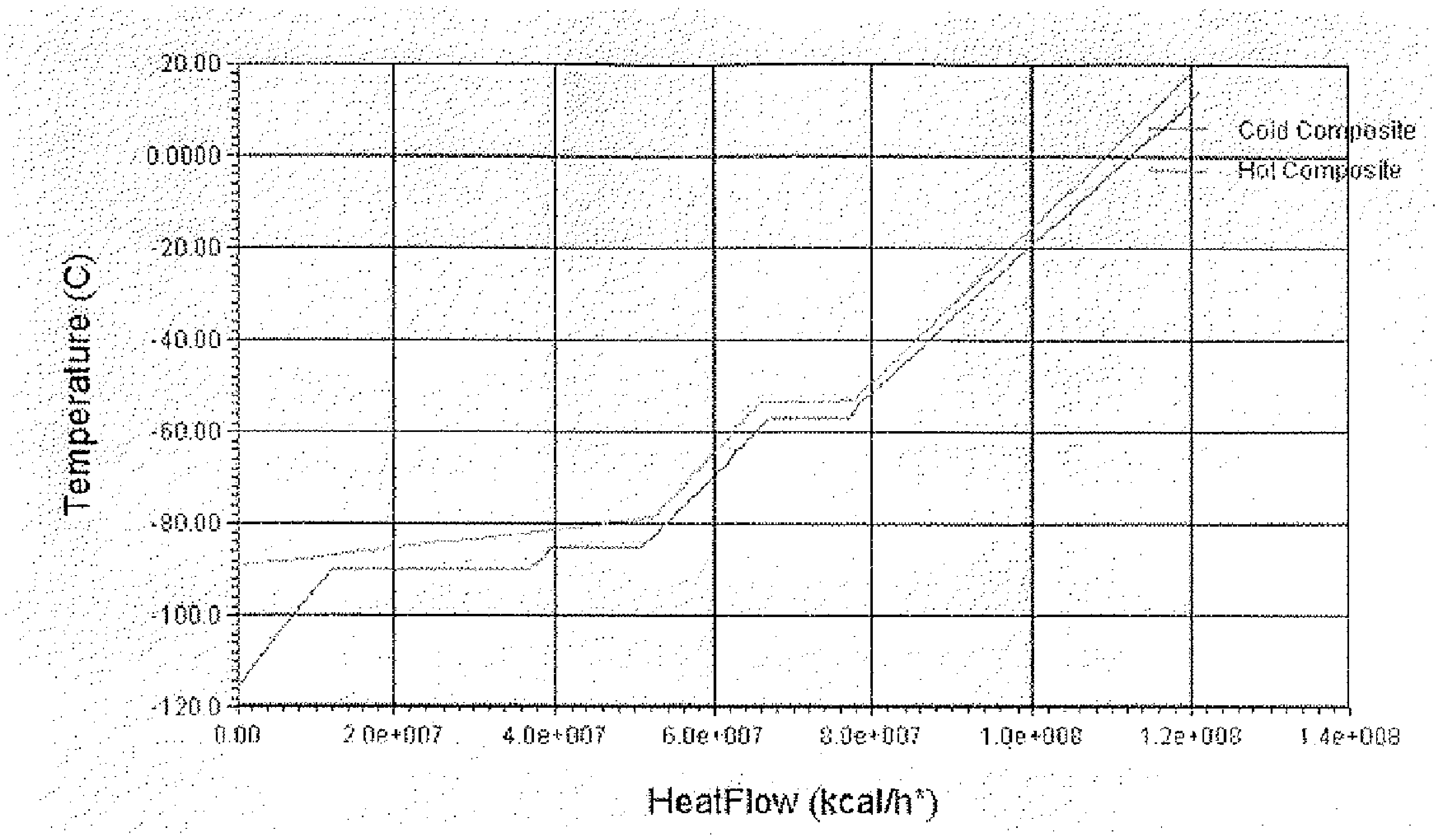
1.4e+008
HeatFlow (kcal/h*)
Cold Composite
Hot Composite

Figure 1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6.0e+007
8.0e+007
1.0e+008
1.2e+008
1.4e+008
HeatFlow (kcal/h*)
Cold Composite
Hot Composite

Figure 2

PROCESS FOR REMOVING CARBON DIOXIDE FROM A GAS STREAM USING DESUBLIMATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/497,148, filed Jun. 15, 2011.

FIELD OF THE INVENTION

[0002] The present invention relates to a cost effective, efficient process for capturing carbon dioxide from a gas stream using desublimation.

BACKGROUND

[0003] The emission of carbon dioxide from fossil fuel combustion is a growing source of concern around the world. Numerous technologies have been developed to address this problem. Research and development continue in this area. One avenue of research has concentrated on the capture of carbon dioxide from flue gas and other gas streams. Some of the major technologies utilized have included amine washes, physical adsorption technologies, cryogenic technologies (carbon dioxide liquefaction) and such. However, these technologies involve significant additional investment and operating costs for industrial plants. For example, in the case of coal power plants a resulting increase of the cost of electricity in the range of 4 to 5 U.S. cents/kWh is expected.

[0004] One possible alternative to traditional capture solutions which is described in literature is called anti-sublimation. This process basically involves separating carbon dioxide from a flue gas by cooling the flue gas to turn the carbon dioxide into a solid (de-sublimation or cryo-condensation of carbon dioxide). Indeed, at such low carbon dioxide partial pressure (<5.11 atmosphere), the carbon dioxide will be directly changed from a gas phase to a solid phase. There exist two main approaches to implement such a process. The first of these approaches involves de-sublimation at atmospheric or very low pressure. With this first approach, a significant external refrigeration loop is required to perform such a cooling (indirect de-sublimation). The second approach is de-sublimation at higher pressure by expansion with solid formation (direct de-sublimation).

[0005] De-sublimation has been described extensively in the literature. See, for example, Cost Analysis of CO_2 Capture by Antisublmation Applied For Coast Fired Boilers, CCT 2007, 16 May 2007; FR 2851936; FR 2820052; FR 2894838; WO 05082493; JP 2000317302; WO 09047341; FR 2867092; WO 09070785; JP 2004286348; WO 06062595; U.S. 6082133; EP 1754695; WO 08095258; AU 2003201393; AU 2003270123; and WO 09070785.

[0006] With regard to the two approaches noted, the first approach is the simplest approach but has several drawbacks. The second approach has shown to be more attractive in terms of energy efficiency, for two main reasons: direct cooling can improve efficiency and there are less pressure drops because of the higher pressure. However, there is no mention in the literature of a process that would simultaneously work at a relatively low pressure and require no external refrigeration. Indeed, although the need of external refrigeration is drastically reduced by the second approach, a small external refrigeration loop is usually needed. This external loop adds equipment and decreases the overall efficiency of the process.

[0007] Accordingly, there exists a need to reduce the cost of carbon dioxide capture from flue gas through improved efficiencies and reduced capital expenditures.

SUMMARY OF THE INVENTION

[0008] The present invention relates to a highly efficient auto-refrigerated process for de-sublimation of a flue gas. In this process, the flue gas is first compressed to a medium range. This compressed flue gas is then cooled before being subjected to a partial desublimation to produce solid carbon dioxide and cold medium pressure flue gas. The solid carbon dioxide is then separated from the cold medium pressure flue gas. The cold medium pressure flue gas is then introduced into an expansion turbine where additional solid carbon dioxide is formed and the pressure of the flue gas is dropped to a low range. This additional solid carbon dioxide is then separated from the low pressure flue gas to produce a carbon dioxide depleted flue gas. The low pressure carbon dioxide depleted flue is gas heated to recover sensible heat. The solid carbon dioxide is split into at least two streams with part of the solid carbon dioxide being brought to or above triple point pressure and liquefied. Sensible heat of the solid and the liquid is recovered as well as fusion heat of the solid when liquefied. The remaining part of the solid is brought to lower pressure (sub-atmospheric pressure) and vaporized at low pressure. Sublimation heat of the low pressure carbon dioxide is recovered to heat exchange with de-sublimating flue gas. Gaseous sub-atmospheric pressure carbon dioxide is then compressed by sub-atmospheric compression means. A portion of this can be compressed to a pressure high enough to be condensed at ambient temperature and then pumped to final pressure. The remaining part can be compressed to an intermediate pressure and condensed at a lower pressure by heat exchange with the rest of the process.

[0009] The invention is also directed to a process for removing carbon dioxide from a carbon dioxide containing gas stream, said process comprising the steps of: a) compressing the carbon dioxide containing gas stream to a pressure that ranges from about 1.1 bar absolute to about 20.0 bar absolute to produce a compressed gas stream; b) routing the compressed gas stream through a main heat exchange system comprising one or more main heat exchangers where the temperature of the compressed gas stream is reduced to a point that a portion of the carbon dioxide in the compressed gas stream is transformed into solid carbon dioxide with the remainder of the carbon dioxide remaining in gaseous form; c) separating the solid carbon dioxide from the compressed cooled gas stream to form a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream; d) introducing the cooled partially carbon dioxide depleted gas stream into an expansion turbine in order to transform additional carbon dioxide within the gas stream into additional solid carbon dioxide; e) separating the additional solid carbon dioxide from the cooled partially carbon dioxide depleted gas stream to form an additional stream of solid carbon dioxide and an expanded carbon dioxide depleted gas stream; f) routing the expanded carbon dioxide depleted gas stream back through the main heat exchange system where the expanded carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. to recover sensible heat and then venting the carbon dioxide depleted gas stream that is withdrawn from the heat exchanger; and g) using the streams of solid carbon dioxide produced to reduce the temperature of the compressed gas stream in step b) by: i) subjecting a portion of the solid carbon dioxide to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel in communication with the main heat exchange system to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat; ii) vaporizing a portion of the solid carbon dioxide in a second vessel in communication with the main heat exchange system at sub-atmospheric pressure to produce a sub-atmospheric pressure carbon dioxide gas and recovering at least sublimation heat; and iii) compressing the sub-atmospheric pressure carbon dioxide gas obtained to produce a compressed carbon dioxide stream.

[0010] The invention is also directed to a process for removing carbon dioxide from a carbon dioxide containing gas stream, said process comprising the steps of: A) routing the carbon dioxide containing gas stream through a main heat exchange system comprising one or more heat exchangers where the temperature of the gas stream is reduced to a point that a portion of the carbon dioxide in the gas stream is transformed into solid carbon dioxide with the remainder of the carbon dioxide remaining in gaseous form, the carbon dioxide containing gas stream having a pressure from about 0.8 to 3.0 bar absolute; B) separating the solid carbon dioxide from the cooled carbon dioxide containing gas stream to form a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream; C) routing the cooled partially carbon dioxide depleted gas stream back through the main heat exchange system where the cooled partially carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. to recover sensible heat and then venting the carbon dioxide depleted gas stream that is withdrawn from the heat exchanger; and D) using the stream of solid carbon dioxide produced to reduce the temperature of the carbon dioxide containing gas stream in step b) by: i) subjecting a portion of the solid carbon dioxide to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel in communication with the main heat exchange system to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat; ii) vaporizing a portion of the solid carbon dioxide in a second vessel in communication with the main heat exchange system at sub-atmospheric pressure to produce a sub-atmospheric pressure carbon dioxide gas and recovering at least sublimation heat; and iii) compressing the sub-atmospheric pressure carbon dioxide gas obtained to produce a compressed carbon dioxide stream.

[0011] The invention may include one or more of the following aspects:

[0012] the portion of solid carbon dioxide subjected to a pressure that is equal to or greater than the triple point pressure of carbon dioxide to produce a carbon dioxide liquid stream is obtained from step b).

[0013] at least a portion of the solid carbon dioxide vaporized at sub-atmospheric pressure to recover at least the sublimation heat and produce a sub-atmospheric pressure carbon dioxide gas is obtained from step d).

[0014] prior to step g), the solid carbon dioxide of step b) and step d) is combined for use in step g).

[0015] the carbon dioxide containing gas stream is a flue gas stream.

[0016] in step e), the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures.

[0017] the vaporization of the solid carbon dioxide with at least two different sub-atmospheric pressures is performed in at least two independent vessels with each independent vessel corresponding to a different sub-atmospheric pressure.

[0018] the vessels are in thermal communication with the main heat exchange system through a series of pipes that run through the main heat exchange system and the various vessels.

[0019] the recovery of the sublimation heat is carried out by circulating one or more fluids between the main heat exchange system and the vessels to recover cold from the phase changes in the vessels and release this cold in the main heat exchange system.

[0020] the one or more fluids are circulated by pumping the one or more fluids or by thermo-siphoning.

[0021] the one or more fluids are selected from CF_4, NF_3, C_2H_6

[0022] the compressed carbon dioxide stream is further treated to obtain the desired carbon dioxide product.

[0023] the carbon dioxide liquid stream is further treated to obtain the desired carbon dioxide product.

[0024] from 90 to 99% of the carbon dioxide in the carbon dioxide containing gas stream is separated by de-sublimination with no external refrigeration cycle.

[0025] the latent heat of fusion for the liquefaction of the solid carbon dioxide in step g i is obtained from condensation of gaseous carbon dioxide in the stream of compressed carbon dioxide stream obtained from step g iii.

[0026] no external source of refrigeration is utilized.

[0027] the carbon dioxide containing stream is compressed prior to being routed into the main heat exchanger in order to have a pressure from about 1.1 to 3.0 bar absolute.

[0028] the carbon dioxide containing gas stream is a flue gas stream.

[0029] in step D), the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures.

[0030] the latent heat of fusion for the liquefaction of the solid carbon dioxide in step D i is obtained from condensation of gaseous carbon dioxide in the stream of compressed carbon dioxide stream obtained from step D iii.

DESCRIPTION OF THE FIGURES

[0031] FIG. **1** presents a detailed example of such a process that have been calculated using process modeling tools and other carbon dioxide gas properties (solid phase properties, sublimation, fusion . . .).

[0032] FIG. **2** presents the associated main heat exchanger diagram (temperature versus heat flow).

DETAILED DESCRIPTION OF THE INVENTION

[0033] The present process relates to a more efficient process for the removal of carbon dioxide from a carbon dioxide containing stream. By capturing the energy associated with the transition of solid carbon dioxide to either a liquid or vapor, it is possible to eliminate or at least significantly minimize the use of the external cooling systems such as additional refrigerant loops including compressors as well as the cooling means for compressed refrigerant that have previously been used in the prior art systems of carbon dioxide removal. The process may be carried out in a direct manner in which the use of the prior art external cooling systems are eliminated or in an indirect manner in which the prior art external cooling systems are minimized (used only to bolster the process).

[0034] With regard to the carbon dioxide containing gas streams that may be treated utilizing either embodiment of the present invention, such streams may be provided from a variety of sources, including but not limited to, flue gas streams, steam methane reforming syngas streams, pressure swing adsorption tail gas streams, gasification streams, carbon dioxide contaminated natural gas streams, metal treatment furnace streams, or refinery streams. The present invention is considered to be particularly advantageous with regard to the treatment of carbon dioxide containing streams which are considered to have low concentrations of carbon dioxide. As used herein, the phrase "low concentrations of carbon dioxide" refers to those carbon dioxide containing streams that have less than 50% carbon dioxide (as measured by molar fraction), especially those carbon dioxide containing streams that have equal to or less than 30%. One particularly preferred carbon dioxide containing gas for treatment with the present process is a flue gas stream having less than or equal to 30% carbon dioxide.

[0035] The first embodiment of the present invention involves the direct manner of removing carbon dioxide from carbon dioxide containing streams without the need to include an external cooling system. The first step of the process involves compressing a carbon dioxide containing gas stream obtained from any of the sources defined hereinbefore to a pressure that ranges from about 1.1 bar to about 20.0 bar absolute in order to obtain a compressed gas stream. In one alternative, the pressure may range from about 2.0 bar absolute to about 16.0 bar absolute. In a still further alternative, the pressure may range from about 3.0 bar absolute to about 10.0 bar absolute. The actual level of compression needed may be achieved by any means known in the art such as by utilizing a compressor. In addition, while the term "a compressor" is utilized, the degree of compression may also be achieved by utilizing more than one compressor (multiple compressors in series). This compression can be isothermal (several stages with inter-stage cooling) or adiabatic (no or less inter-stage cooling but heat recovery of the heat from the hot pressurized gas stream in a steam cycle). Also, in the instance that the carbon dioxide containing gas is already within this compression level (where the source from which the carbon dioxide containing gas is obtained produces a carbon dioxide containing gas that is already at a pressure level as noted), it may be possible to eliminate this step.

[0036] Once the compressed gas stream is achieved, this gas stream is routed through a main heat exchange system where the temperature of the compressed gas stream is reduced to a point that a portion of the carbon dioxide in the compressed gas stream is transformed into solid carbon dioxide while the remainder of the carbon dioxide in the carbon dioxide containing gas stream remains in gaseous form. A variety of different types of heat exchangers for carrying out processes such as those of the present invention are commercially available. Such heat exchangers are typically referred to as multiple zone heat exchangers. Note that the present invention is not meant to be limited with regard to the particular type of heat exchanger utilized in the main heat exchange system provided that the heat exchange system has multiple zones. Alternatively, in the present invention the function of main heat exchange system could be carried out by several heat exchangers, in parallel and/or in series. In particular, those skilled in the art will recognize that it can be advantageous to separate heat exchange in several heat exchangers to simplify the heat exchangers as well as separate the different functions requiring different technologies. Regardless of the specific type of main heat exchange system utilized, in the case of multiple heat exchange zones or multiple heat exchangers, the multiple heat exchange zones or multiple heat exchangers may be thermally integrated with one another. This means that they are intentionally designed to achieve heat transfer between one another.

[0037] As noted, the temperature of the compressed gas stream is reduced to a point that a portion of the carbon dioxide contained in the compressed gas stream is transformed into solid carbon dioxide. More specifically, this transformation from a gas to a solid with no intervening liquid form is typically referred to as cryo-condensation, anti-sublimation or de-sublimation. Sublimation, the opposite of deposition or de-sublimation refers to the change of carbon dioxide from a solid to a gas with no intervening liquid form. Note that at temperatures below −56.6° C. and pressures below 5.11 atm (the triple point), sublimation/de-sublimation occurs. At atmospheric pressure, this temperature is −78.5° C.

[0038] De-sublimation occurs within the main heat exchange system as the gas stream passes through the main heat exchange system. Once the de-sublimation occurs, the compressed gas stream that exits the main heat exchange system includes some carbon dioxide that is in solid form and some carbon dioxide that is in gaseous form. Accordingly, the next step in the process is to separate the solid carbon dioxide from the compressed cooled gas stream thereby forming a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream. With regard to the present invention, the phrase "solid carbon dioxide" refers to the carbon dioxide produced in solid form due to the de-sublimation. This solid carbon dioxide will typically appear in form like a powdering of snow. In addition, the phrase "stream of solid carbon dioxide" refers to the individual bits or particles of carbon dioxide that when separated from the compressed cooled gas stream are considered to form a "stream" of the solid carbon dioxide particles. The compressed gas stream that includes some carbon dioxide that is in solid form can be separated into a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas by any separation method known in the art. Typically, as the compressed gas stream that includes some carbon dioxide in solid form exits the main heat exchange system, the compressed gas stream is passed through a cyclone in order to separate the solids from the gases. In an alternative case, the separation can be performed simultaneously with the de-sublimation. For instance, solid carbon dioxide can be allowed to settle or fall out of the gas stream as the gas stream passes along thereby resulting in the separation (see for example WO 2010/107820).

[0039] After the stream of solid carbon dioxide and the cooled partially carbon dioxide depleted gas are obtained, the cooled partially carbon dioxide depleted gas stream is introduced into an expansion turbine. Any expansion turbine known in the art may be utilized in the present process to transform at least a portion of the remainder of the carbon dioxide found within the cooled partially carbon dioxide depleted gas stream into additional solid carbon dioxide. In addition, those skilled in the art will recognize that a series of expansion turbines may also be utilized to carry out this transformation. The expansion turbine could also have a specific design in order to meet the specific requirements of handling solid formation. As the cooled partially carbon dioxide depleted gas stream is passed through the expansion turbine, the gas stream expands thereby resulting in a cooling of the gas stream and the transformation of part of the carbon dioxide in the gas stream from a gaseous state into a solid state. While the phrase "remainder of the carbon dioxide" is utilized with regard to the description of the process, it should be noted that the process of the present invention, while ultimately seeking to remove close to 100% of the carbon dioxide present in the original carbon dioxide containing gas stream, will often result in some of the gaseous form carbon dioxide remaining in the resulting expanded carbon dioxide depleted gas stream. Typically, it is possible to remove from 90 to 99% of the carbon dioxide present in the original carbon dioxide containing gas stream thereby resulting in an expanded carbon dioxide depleted gas stream which actually contains from 0.1 to 10% (molar percent) of carbon dioxide with the preference being that the amount remaining be between about 0.1% and about 2.0%.

[0040] The separation of the additional solid carbon dioxide from the cooled partially carbon dioxide depleted gas stream to form an additional stream of solid carbon dioxide and an expanded carbon dioxide depleted gas stream can be carried out in the same manner as noted above with regard to the separation of the solid carbon dioxide from the compressed cooled gas stream to form a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream. More specifically, the additional solid carbon dioxide from the cooled partially carbon dioxide depleted gas stream utilization any separation means that are known in the art for separating solids from gases including the use of a cyclone. The expansion is carried out to achieve a gas stream that is down to a pressure from about 1.0 bar absolute to about 3.0 bar absolute, preferably close to atmospheric pressure, more specifically approximately 1.3 bar absolute. Note the preference of 1.3 bar absolute is to compensate for any pressure drops occurring after the turbine in order to vent as close as possible to atmospheric pressure.

[0041] The expanded carbon dioxide depleted gas stream that is obtained is then routed back through the main heat exchange system where the expanded carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. in order to recover sensible heat. As used herein, the term “sensible heat” refers to the heat or energy produced due to the change in temperature. Once the carbon dioxide depleted gas stream is passed through the main heat exchange system, it is withdrawn and vented to the atmosphere.

[0042] The streams of solid carbon dioxide that are produced are then utilized to reduce the temperature of the compressed gas stream as noted hereinbefore. This is accomplished by first subjecting a portion of the solid carbon dioxide obtained to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat. Note that the first vessel can be any vessel known in the art that is sufficient to allow for the subjecting of the solid carbon dioxide to the noted pressure. Accordingly, as used herein with regard to the present process, the term “vessel” is not meant to be restrictive and is simply utilized to denote where the solid carbon dioxide is subjected to the conditions noted. Non-limiting examples of such vessels include, but are not limited to any kind of storage tanks (vertical, horizontal or spherical). The first vessel is configured in such a manner that it is in communication with the main heat exchanger in order to recover fusion heat and sensible heat. While this communication can be in any manner known in the art, typically the communication will be through a series of pipes that run through the main heat exchange system and the first vessel. More specifically, the series of pipes will run through at least one of the at least one heat exchanger of the main heat exchange system and through the first vessel. As sublimation occurs in the first vessel (the transformation of the solid carbon dioxide to gaseous carbon dioxide), the sensible heat and the fusion heat are recovered by circulating one or more fluids through the pipes between the main heat exchange system and the first vessel. This allows for the recovery of cold due to the phase changes in the first vessel and the release of this cold in the main heat exchange system.

[0043] In the next step of the process, a portion of the solid carbon dioxide is vaporized in a second vessel that is also in communication with the main heat exchange system. This vaporization occurs at sub-atmospheric pressure to allow for the production of a sub-atmospheric pressure carbon dioxide gas and the recovery of at least sublimation heat. In an alternative schematic, the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures. When the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures, the vaporization is carried out in at least two independent vessels with each independent vessel corresponding to a different sub-atmospheric pressure.

[0044] As noted with regard to the first vessel, the second vessel, as well as any other vessels that might be utilized, are in communication with the main heat exchange system through a series of pipes that run through the main heat exchange system and the various vessels. By circulating one or more fluids through these pipes between the main heat exchange system and the various vessels it is possible to recover cold from the phase changes in the vessels and release this cold in the main heat exchange system. The one or more fluids in the pipes are typically circulated using any method that is known in the art, for example, by pumping the one or more fluids or by thermo-siphoning. Typically, the one or more fluids are selected from CF_4, NF_3, C_2H_6 although other fluids that are known in the art for such purposes may be utilized.

[0045] The sub-atmospheric pressure carbon dioxide gas obtained is compressed to produce a compressed carbon dioxide stream. This compressed carbon dioxide stream is further treated by any methods known in the art to obtain the desired carbon dioxide product. In addition, the carbon dioxide liquid stream is further treated to obtain the desired carbon dioxide product. For example, the desired product could be: under liquid conditions in which case the liquid would require limited further treatment and the gas would require at least compression and then cooling; or under super-critical conditions where the liquid would require at least further compression and/or pumping and the gas would require at least further compression and cooling. Liquefaction of this compressed carbon dioxide stream may also be accomplished through heat exchange with the above-described solid carbon dioxide that is liquefied. In this manner, the heat of vaporization is exchanged with the heat of fusion to condense carbon dioxide into liquid form from the compressed carbon dioxide stream and to liquefy the solid carbon dioxide.

[0046] In the second embodiment of the present process, the carbon dioxide is removed from the carbon dioxide containing streams using an indirect manner. According to this embodiment, the use of an external cooling system is minimized, if not eliminated. The first step of the process involves routing the carbon dioxide containing gas stream though a main heat exchange system comprising one or more heat exchangers where the temperature of the carbon dioxide containing gas stream is reduced to a point that a portion of the carbon dioxide in the carbon dioxide containing gas stream is transformed into solid carbon dioxide (as defined hereinbefore) while the remainder of the carbon dioxide in the carbon dioxide containing gas stream remains in gaseous form. Note that when the carbon dioxide containing gas stream is introduced into the main heat exchange system, it is introduced at a pressure that ranges from about 1.1 bar to about 3.0 bar absolute, preferably from about 1.1 bar absolute to about 2.0 bar absolute. In those instances where the carbon dioxide containing gas stream to be utilized is not within this pressure range, the carbon dioxide containing gas stream is first compressed in one or more compressors to achieve this level of pressure as described hereinbefore with regard to the first embodiment.

[0047] As noted hereinbefore, a variety of different types of heat exchangers are available for the main heat exchange system of the processes of the present invention such as multiple zone heat exchangers in parallel and/or series. This embodiment, as with the previous embodiment, is not meant to be limited with regard to the particular type of heat exchanger utilized provided that the heat exchanger has multiple zones. The multiple zones may be thermally integrated with one another. As the carbon dioxide containing gas stream is routed through the main heat exchange system, the temperature of the carbon dioxide containing gas stream is reduced to a point that a portion of the carbon dioxide contained in the compressed gas stream is transformed into solid carbon dioxide with no intervening liquid form. Once the de-sublimation occurs, the gas stream that exits the main heat exchange system includes some carbon dioxide that is in solid form and some carbon dioxide that is in gaseous form. Accordingly, the next step in the process is to separate the solid carbon dioxide from the cooled carbon dioxide containing gas stream thereby forming a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream. The carbon dioxide containing gas stream that includes some carbon dioxide that is in solid form can be separated into a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream by any separation method known in the art including through a cyclone or by allowing the solid to settle or fall out of the gas stream after the gas stream exits the main heat exchange system.

[0048] After the stream of solid carbon dioxide and the cooled partially carbon dioxide depleted gas are obtained, the cooled partially carbon dioxide depleted gas stream is then routed back through the main heat exchange system where the cooled partially carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. in order to recover sensible heat as defined hereinbefore. Once the carbon dioxide depleted gas stream is passed through the main heat exchange system, it is withdrawn and vented to the atmosphere.

[0049] The stream of solid carbon dioxide that is produced is used to reduce the temperature of the carbon dioxide gas stream as noted hereinbefore by first subjecting a portion of the solid carbon dioxide obtained to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel as defined hereinbefore to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat. The first vessel is configured in such a manner that it is in communication with the main heat exchange system in order to recover fusion heat and sensible heat, typically through a series of pipes that run through the main heat exchange system and the first vessel. As melting occurs in the first vessel (the transformation of the solid carbon dioxide to liquid carbon dioxide), the sublimation heat and the fusion heat are recovered by circulating one or more fluids through the pipes between the main heat exchange system and the first vessel thereby allowing for the recovery of cold due to the phase changes in the first vessel and the release of this cold in the main heat exchange system. Alternatively, the solid carbon dioxide may be liquefied through heat exchange with a gaseous carbon dioxide stream in a separate heat exchange system. As the solid carbon dioxide receives the heat of fusion from the gaseous carbon dioxide stream, the gaseous carbon dioxide is condensed to liquid.

[0050] In the next step of the process, a portion of the solid carbon dioxide is vaporized at sub-atmospheric pressure in a second vessel that is also in communication with the main heat exchange system. This allows for the production of a sub-atmospheric pressure carbon dioxide gas and the recovery of at least sublimation heat. In an alternative schematic, the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures in at least two independent vessels with each independent vessel corresponding to a different sub-atmospheric pressure.

[0051] The various vessels are in communication with the main heat exchange system through a series of pipes that run through the main heat exchange system and the various vessels. By circulating one or more fluids through these pipes between the main heat exchange system and the various vessels it is possible to recover cold from the phase changes in the vessels and release this cold in the main heat exchange system. The one or more fluids in the pipes are typically circulated using any method that is known in the art, for example, by pumping the one or more fluids or by thermo-siphoning. Typically, the one or more fluids are selected from CF_4, NF_3, C_2H_6 although other fluids that are known in the art for such purposes may be utilized.

[0052] In this embodiment, the sub-atmospheric pressure carbon dioxide gas obtained is compressed to produce a compressed carbon dioxide stream. This compressed carbon dioxide stream is further treated by any methods known in the art to obtain the desired carbon dioxide product. In addition with regard to this embodiment, the carbon dioxide liquid stream is further treated to obtain the desired carbon dioxide product.

[0053] The first embodiment of the present process will be further described with regard to FIG. **1**. Note that this figure is in no way meant to be limiting with regard to the process of the present invention. In FIG. **1**, a flue gas stream (**1**) is first compressed in a compressor (**2**) to a pressure between about 1.1 bar absolute and 20.0 bar absolute, preferably to approximately 6.0 bar absolute. This compression can be isothermal (several stages with inter-cooling; not shown) or adiabatic (no or less inter-cooling but heat recovery of the heat from the hot pressurized flue gas in the steam cycle). After cooling to ambient conditions the pressurized flue gas stream (**1.1**) enters a main heat exchanger (**3**) and is cooled down to approximately −90° C. thereby forming solid carbon dioxide within the gaseous flue gas stream (**1.1**). This cryocooled gas stream (**1.2**) that comprises solid carbon dioxide, gaseous carbon dioxide and the remaining components of the flue gas stream then exists the main heat exchanger (**3**) and the part of the carbon dioxide stream that has been de-sublimated (**5**) is separated from the rest of the flue gas stream (**4**). This cold partially carbon dioxide depleted flue gas stream (**4**) is then expanded through an expansion turbine (**6**) down to close to atmospheric pressure (approximately **1.3** bar absolute) where more solid carbon dioxide is formed As the stream exits the expansion turbine (**6**), the additional solid carbon dioxide (**8**) is separated from the remaining portion of gas stream (**4**) to form an expanded carbon dioxide depleted gas stream (**10**). The carbon expanded carbon dioxide depleted gas stream (**10**) is then routed back through the main heat exchanger (**3**) to be heated in the main heat exchanger (**3**) in order to recover cold before venting the gas stream (**11**) at close to ambient temperature.

[0054] The first solid carbon dioxide stream (**5**) is entered in a first vessel (**7**) that is maintained at a pressure close to the triple point of carbon dioxide. By direct or indirect heat exchange, part of the first solid carbon dioxide stream (**5**) is heated and liquefied in this vessel (**7**) to provide cold in the line (**7.1**) that runs through the main heat exchanger (**3**). The resulting liquid is then pumped (**21**) to recover sensible heat from the liquid up to about 10° C. in the line (**7.1**) of the main heat exchanger (**3**). The resulting stream (**23**) is mixed with other streams to be the final carbon dioxide product. The remaining part of the solid is entered in the second vessel (**9**) after it's pressure has been reduced.

[0055] The second solid carbon dioxide stream (**8**) is sent to the second vessel (**9**) after reducing the pressure down to about 585 mbar absolute. By direct or indirect heat exchange, part of the solid carbon dioxide stream (**8**) is heated and vaporized in this vessel (**9**) to provide cold in the line (**9.1**) of the main heat exchanger (**3**). The resulting gas stream (**11**) is recovered at −55° C. for compression. The remaining part of the solid carbon dioxide stream (**8**) is entered in a third vessel (**10**) after reducing the pressure of the remaining part of the solid carbon dioxide stream (**8**). The third vessel (**10**) is maintained at a pressure of approximately 375 mbar absolute. By direct or indirect heat exchange, part of the solid carbon dioxide stream (**8**) is heated and vaporized in this vessel (**10**) to provide cold in the line (**10.1**) of the main heat exchanger (**3**). The resulting gas stream (**12**) is recovered at −55° C. for compression in vacuum pressuring equipment (**13**). It is then mixed with gas stream **11** and compressed again by one or several stages of additional compression including vacuum pressuring equipment again (**14**). Part of the partially compressed carbon dioxide stream (**16**) is sent at a pressure of approximately 6.0 bar absolute in the line (**16.1**) of the main heat exchanger (**3**) in ordered to be condensed and recovered as a liquid in a separator (**17**). The resulting liquid is then pumped (**22**) to recover sensible heat from the liquid up to 10° C. in the line (**22.1**) of the main heat exchanger (**3**). The resulting stream (**19**) is mixed with other streams to be the final carbon dioxide product.

[0056] The remaining part of the partially compressed carbon dioxide (**24**) is further compressed (**15**) up to 60 bar and then condensed at ambient conditions (**18**), typically using available cooling water. It is then mixed with streams **19** and **23** to be pumped to its final pressure (for example to 150 bar absolute for pipeline transport).

[0057] The above is only one of the many examples of the present process using the described invention. For instance, the use of a single line for heat exchange may not be convenient, especially in terms of handling solids. In addition, the process describes the heat exchange as occurring in one main heat exchanger but the present process is also contemplated to be formulated to be divided in one de-sublimating heat exchanger and several other heat recovery heat exchangers.

[0058] The heat exchange between the three vessels can be done directly or indirectly. For example a fluid could be circulated between the said vessels and the main heat exchanger(s). This fluid could be for example a liquid circulated by a pump or an evaporating liquid (vaporization in the heat exchanger and condensation in the vessel) also circulated by a pump under the liquid phase. This fluid could be any fluid able to condense/vaporize at the desired pressures and temperatures and could be one different fluid for each vessel.

What is claimed is:

1. A process for removing carbon dioxide from a carbon dioxide containing gas stream, said process comprising the steps of:

a. compressing the carbon dioxide containing gas stream to a pressure that ranges from about 1.1 bar absolute to about 20.0 bar absolute to produce a compressed gas stream;

b. routing the compressed gas stream through a main heat exchange system comprising one or more main heat exchangers where the temperature of the compressed gas stream is reduced to a point that a portion of the carbon dioxide in the compressed gas stream is transformed into solid carbon dioxide with the remainder of the carbon dioxide remaining in gaseous form;

c. separating the solid carbon dioxide from the compressed cooled gas stream to form a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream;

d. introducing the cooled partially carbon dioxide depleted gas stream into an expansion turbine in order to transform additional carbon dioxide within the gas stream into additional solid carbon dioxide;

e. separating the additional solid carbon dioxide from the cooled partially carbon dioxide depleted gas stream to form an additional stream of solid carbon dioxide and an expanded carbon dioxide depleted gas stream;

f. routing the expanded carbon dioxide depleted gas stream back through the main heat exchange system where the expanded carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. to recover sensible heat and then venting the carbon dioxide depleted gas stream that is withdrawn from the heat exchanger;

g. using the streams of solid carbon dioxide produced to reduce the temperature of the compressed gas stream in step b) by: i) subjecting a portion of the solid carbon dioxide to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel in communication with the main heat exchange system to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat; ii) vaporizing a portion of the solid carbon dioxide in a second vessel in communication with the main heat exchange system at sub-atmospheric pressure to produce a sub-atmospheric pressure carbon dioxide gas and recovering at least sublimation heat; and iii) compressing the sub-atmospheric pressure carbon dioxide gas obtained to produce a compressed carbon dioxide stream.

2. The process of claim **1**, wherein the portion of solid carbon dioxide subjected to a pressure that is equal to or greater than the triple point pressure of carbon dioxide to produce a carbon dioxide liquid stream is obtained from step b).

3. The process of claim **1**, wherein at least a portion of the solid carbon dioxide vaporized at sub-atmospheric pressure to recover at least the sublimation heat and produce a sub-atmospheric pressure carbon dioxide gas is obtained from step d).

4. The process of claim **1**, wherein prior to step g), the solid carbon dioxide of step b) and step d) is combined for use in step g).

5. The process of any claim **1**, wherein the carbon dioxide containing gas stream is a flue gas stream.

6. The process of claim **1**, wherein in step e), the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures.

7. The process of claim **6**, wherein the vaporization of the solid carbon dioxide with at least two different sub-atmospheric pressures is performed in at least two independent vessels with each independent vessel corresponding to a different sub-atmospheric pressure.

8. The process of claim **7**, wherein the vessels are in thermal communication with the main heat exchange system through a series of pipes that run through the main heat exchange system and the various vessels.

9. The process of claim **8**, wherein the recovery of the sublimation heat is carried out by circulating one or more fluids between the main heat exchange system and the vessels to recover cold from the phase changes in the vessels and release this cold in the main heat exchange system.

10. The process of claim **9**, where the one or more fluids are circulated by pumping the one or more fluids or by thermo-siphoning.

11. The process of claim **10**, wherein the one or more fluids are selected from CF_4, NF_3, C_2H_6

12. The process of claim **1**, wherein the compressed carbon dioxide stream is further treated to obtain the desired carbon dioxide product.

13. The process of claim **1**, wherein the carbon dioxide liquid stream is further treated to obtain the desired carbon dioxide product.

14. The process of claim **1**, wherein from 90 to 99% of the carbon dioxide in the carbon dioxide containing gas stream is separated by de-sublimination with no external refrigeration cycle.

15. The process of claim **1**, wherein the latent heat of fusion for the liquefaction of the solid carbon dioxide in step g i is obtained from condensation of gaseous carbon dioxide in the stream of compressed carbon dioxide stream obtained from step g iii.

16. The process of claim **1**, wherein no external source of refrigeration is utilized.

17. A process for removing carbon dioxide from a carbon dioxide containing gas stream, said process comprising the steps of:

- a. routing the carbon dioxide containing gas stream through a main heat exchange system comprising one or more heat exchangers where the temperature of the gas stream is reduced to a point that a portion of the carbon dioxide in the gas stream is transformed into solid carbon dioxide with the remainder of the carbon dioxide remaining in gaseous form, the carbon dioxide containing gas stream having a pressure from about 0.8 to 3.0 bar absolute;
- b. separating the solid carbon dioxide from the cooled carbon dioxide containing gas stream to form a stream of solid carbon dioxide and a cooled partially carbon dioxide depleted gas stream;
- c. routing the cooled partially carbon dioxide depleted gas stream back through the main heat exchange system where the cooled partially carbon dioxide depleted gas stream is heated to a temperature that ranges from about −20° C. to about 50° C. to recover sensible heat and then venting the carbon dioxide depleted gas stream that is withdrawn from the heat exchanger; and
- d. using the stream of solid carbon dioxide produced to reduce the temperature of the carbon dioxide containing gas stream in step b) by: i) subjecting a portion of the solid carbon dioxide to a pressure that is equal to or greater than the triple point pressure of carbon dioxide in a first vessel in communication with the main heat exchange system to produce a carbon dioxide liquid stream and recovering fusion heat and sensible heat; ii) vaporizing a portion of the solid carbon dioxide in a second vessel in communication with the main heat exchange system at sub-atmospheric pressure to produce a sub-atmospheric pressure carbon dioxide gas and recovering at least sublimation heat; and iii) compressing the sub-atmospheric pressure carbon dioxide gas obtained to produce a compressed carbon dioxide stream.

18. The process of claim **17**, wherein the carbon dioxide containing stream is compressed prior to being routed into the main heat exchanger in order to have a pressure from about 1.1 to 3.0 bar absolute.

19. The process of claim **17**, wherein the carbon dioxide containing gas stream is a flue gas stream.

20. The process of claim **17**, wherein in step d), the vaporization of the solid carbon dioxide is carried out with at least two different sub-atmospheric pressures.

21. The process of claim **20**, wherein the vaporization of the solid carbon dioxide with at least two different sub-atmospheric pressures is performed in at least two independent vessels with each independent vessel corresponding to a different sub-atmospheric pressure.

22. The process of claim **21**, wherein the vessels are in communication with the main heat exchanger through a series of pipes that run through the main heat exchange system and the various vessels.

23. The process of claim **22**, wherein the recovery of the sublimation heat is carried out by circulating one or more fluids between the main heat exchange system and the vessels to recover cold from the phase changes in the vessels and release this cold in the main heat exchange system.

24. The process of claim **23**, where the one or more fluids are circulated by pumping the one or more fluids or by thermo-siphoning.

25. The process of claim **24**, wherein the one or more fluids are selected from CF_4, NF_3, C_2H_6

26. The process of claim **17**, wherein the compressed carbon dioxide stream is further treated to obtain the desired carbon dioxide product.

27. The process of claim **17**, wherein the carbon dioxide liquid stream is further treated to obtain the desired carbon dioxide product.

28. The process of claim **17**, wherein the latent heat of fusion for the liquefaction of the solid carbon dioxide in step D i is obtained from condensation of gaseous carbon dioxide in the stream of compressed carbon dioxide stream obtained from step D iii.

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