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(54) ENERGY GENERATION FROM WASTE HEAT USING THE CARBON CARRIER THERMODYNAMIC CYCLE

(71) Applicant: CLIMEON AB, Danderyd (SE)

(72) Inventor: Joachim Karthauser, Sollentuna (SE)

(73) Assignee: Climeon AB, Danderyd (SE)

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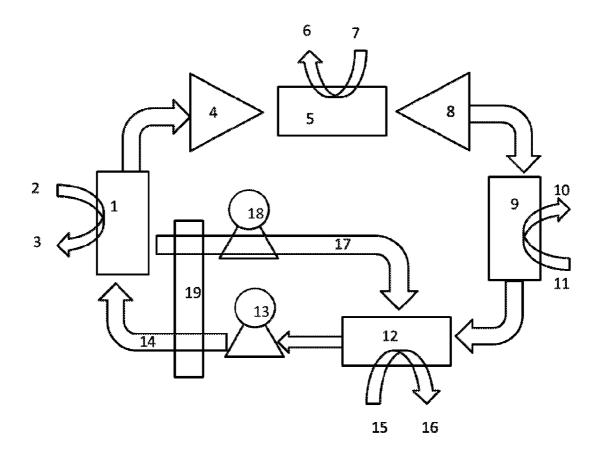
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(57) ABSTRACT

The invention relates to a method is provided which allows the generation of high temperatures, e.g. above 120° C. and maximum 200° C. and low temperatures, e.g. below minimum minus 20° C., from waste heat or geothermal heat or similar heat sources having a temperature of between 20 and 70° C. The method may use essentially pure carbon dioxide as primary working fluid in an essentially closed loop as described in previous disclosures, alternatively low boiling solvents are employed. The common feature of different embodiments is that the system operates at least partly, specifically in the absorber or cold side of the process, below atmospheric pressure (1 bar). In the method a heat pump or heat transformer is realized within the technical boundaries mentioned above. The invention also relates to the use of the method in combination with a district heating system for elevating the temperature of the district heating medium or for electricity production on demand.



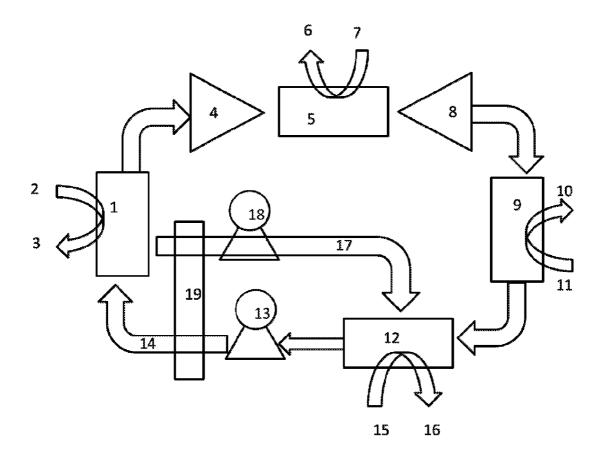


Fig. 1

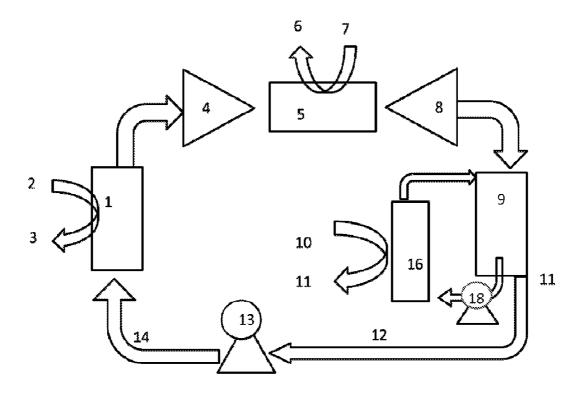


Fig. 2

ENERGY GENERATION FROM WASTE HEAT USING THE CARBON CARRIER THERMODYNAMIC CYCLE

FIELD OF THE INVENTION

[0001] The present invention relates to a method for generation of energy where a heat source supplies thermal energy in the range 30-80° C. to a Rankine cycle including a desorber on the hot side, an absorber or liquefier on the cold side, heat exchangers and at least one compressor and at least one pump for working fluid, and at least one of the following product streams is obtained:

[0002] thermal energy in the range +90, +100, +120 and maximum $+200^{\circ}$ C.,

[0003] thermal energy in the range +15, +10, +5, 0, -5 and minimum -20° C.,

[0004] electricity from the decompression of CO₂ or a working fluid following the extraction of heat.

BACKGROUND OF THE INVENTION

[0005] Reference is made to PCT/SE/2012/050319 or WO 2012/128715 with priority from SE 1100208-6 (filed Mar. 22, 2011), U.S. application 61/468 474 (filed Mar. 28, 2011) and SE 1100596-4 (filed 16.08.2011), these documents are included by way of reference. These documents describe a novel thermodynamic cycle for energy and cold production from heat below 160° C., called C3 or "Carbon Carrier Cycle".

[0006] Reference is also made to SE 1200711-8 and SE 1200554-2 (earliest priority Sep. 11, 2012), now submitted as PCT application. Reference is also made to recent disclosures SE 1400027-7, SE 1400186-1 (turbines), and SE 1400160-6. These disclosures, also included by way of reference, describe various preferred embodiments and improvements of the C3 cycle.

[0007] This invention relates to the field of heat pumps. Essentially, a heat pump uses one part electrical energy to generate more than one, often 3-5 parts thermal energy, e.g. for warming of houses. The ratio of heat energy generated to electrical input energy is called COP or coefficient of performance. Many embodiments are known, e.g. heat pumps which use ground heat of around 10° C. to heat a cold gas which later is compressed and transfers heat to a household water heating system (often between 50-90° C.). The gas, typically being propane, butane or R134a or similar HFC (hydrogen-containing fluorocarbon), is expanded thereby cooling down, for the cycle to start again. Some heat pumps working with CO₂ gas only are also known.

[0008] Examples of prior art are also WO 2006/124776 (DuPont de Nemours), disclosing a heat pump using at least one refrigerant and at least one ionic liquid, preferably both fluorinated, and WO 2004/104399 (Dresser), which discloses the coupling of compressor and expansion device on one rotating shaft as a means of increasing the efficiency of a heat pump or air conditioning machine, see e.g. FIG. 4 in said disclosure.

[0009] The improvement needs for heat pumps are evident from the following: a) Lower paraffins as working fluids are flammable and pose therefore risks. b) The often used HFC are expensive, and whilst they are not dangerous for the earth's ozone layer, they contribute to the greenhouse effect. Emissions to the environment have to be avoided, causing strict regulations and costs for disposal and repair. c) Heat

pumps according to the state-of-the-art operate at relatively high pressure (e.g. above 30 bar), causing high equipment costs. d) For profitable operation of heat pumps, it would be desirable to increase the COP to clearly above 5.

[0010] This text discloses various solutions of said problems and describes different embodiments. The common feature of the different embodiments of the invention is that a low pressure system of high efficiency has been realized whereby the pressures and temperatures in the process are in the following specified ranges:

[0011] Desorber: 0.5-5 bar, 30-80° C.

[0012] Heat exchanger for heat production: 5-50 bar, 100-250° C.,

[0013] Absorber: 0.01-0.9 bar, 10-50° C.

[0014] Specifically the absorber or cold side of the process operates always below atmospheric pressure. It is unexpected and surprising that a system according to the invention can operate reliably as prior art suggests that air ingress and thereby performance deterioration is unavoidable. The system is therefore operated together with a separate device for concentration and ejection of non-condensable gases, see also SE 1400182-0 and 5E1400349-5 (submitted 04 April and 08 July 2014 resp.).

SUMMARY OF THE INVENTION

[0015] The object of the invention is thus achieved by a method for generation of energy where a heat source supplies thermal energy in the range 30-80° C. to a Rankine cycle including a desorber on the hot side, an absorber or liquefier on the cold side, heat exchangers and at least one compressor and at least one pump for working fluid, and at least one of the following product streams is obtained:

[0016] thermal energy in the range +90, +100, +120 and maximum +200 $^{\circ}$ C.,

[0017] thermal energy in the range +15, +10, +5, 0, -5 and minimum -20° C.,

[0018] electricity from the decompression of CO₂ or a working fluid following the extraction of heat,

characterized by that the pressure in the absorber or condenser section are always below 1 bar and that the pressures and temperatures in the process are in the following specified ranges:

[0019] Desorber: 0.5-5 bar, 30-80° C.

[0020] Heat exchanger for heat production: 5-50 bar, 100-250 $^{\circ}$ C.,

[0021] Absorber: 0.01-0.9 bar, 10-50° C.

[0022] Preferred embodiments are defined in the appending dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] The invention is described in more detail below in the form of non-limited examples, reference being made to the appended drawings, in which

[0024] FIG. 1 shows the heat pump according to the invention in one specific embodiment whereby the working fluid comprises CO_2 and amines, and

[0025] FIG. 2 shows a different embodiment whereby the working fluid comprises low boiling solvents with boiling points at atmospheric pressure of 50-100° C.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0026] The heat pump is shown in one embodiment in FIG.

[0027] The heat pump according to the invention operates as follows: heat, e.g. geothermal or waste heat of e.g. 40-70° C., is supplied via heat exchanger (1) (flow in at (2), flow out at (3) to a mixture of CO₂ and absorbent (CO₂-rich absorbent mix). This mixture, as described in the a.m. disclosures and essentially comprising amines (including ammonia, NH₃) and CO₂, e.g. in the form of carbonates or carbamates, is pumped using pump (13) into the heat exchanger through pipe (14). In the desorber (1), CO₂ gas is desorbed at a pressure dependent on the nature of the absorbent, but typically being 0.3 to 2 bar. CO₂ gas is compressed in compressor (4) to a higher pressure, e.g. 5-20 bar, and the CO2 is heated by compression. This heat is extracted in heat exchanger (5), and the heat is transferred to a medium through pipes (6) and (7). The colder gas is expanded through an expansion machine (8) which preferably is mechanically coupled to (4) to save energy. Compression requires electrical energy, decompression delivers energy such that it is desired to minimize the energy requirement. Depending on the configuration, the process from stage (4) to stage (8) (compression and decompression) may deliver (electrical) energy provided the pressure at (1) is higher than at (9). During the decompression at (8) and (9), the CO₂ gas cools down to very low temperature, e.g. minus 50° C. The cold is extracted in heat exchanger (9) using medium flowing through (10) and (11). The gas is further led into absorber (12) where it is combined with CO₂-lean absorbent mix transported through pipe (17) from the desorber (1). An absorption device as described in the a.m. disclosures is used preferably, e.g. a spraying device optionally combined with multiple pass, counter-current absorption, wiped film technology, cooling during absorption etc. It is useful to employ pump (18) to generate the necessary pressure (e.g. 3 bar) to accomplish the ideal spray characteristics, i.e. small droplets of absorbent which react quickly with CO₂ gas from (9). It can be useful to couple pumps (13) and (18) in order to save energy.

[0028] Heat is generated during the chemical reaction of absorbent and CO₂. This heat may be removed using a heat exchanger in combination with the absorber (12). This heat may be discarded or it may be used for pre-heating the CO₂-rich absorbent mix prior to entry into desorber (1), this option is not shown in the figure. The pre-heating is preferably achieved by using a heat exchanger (19) in which hot, lean absorbent in pipe (17) transfers its heat energy to incoming rich absorbent in pipe (14).

[0029] The method allows the construction of small- or large-scale heat pumps. Useful heat source inputs are geothermal sources of 40-70° C., waste heat from power plants, waste heat from the conventional operation of C3 cycle as disclosed previously, and many other heat sources. Various embodiments are conceivable where the operation is adjusted to the waste heat sources available. The chemistries disclosed in a.m. applications describe a range of systems which are useful for various configurations. The high COP can be explained by the fact that, differing from conventional heat pumps, compression energy can partly be recovered in the decompression device.

[0030] Transport of liquids through heat exchangers etc only requires relatively low amounts of energy.

[0031] In summary, a novel heat pump technology is disclosed allowing the use of essentially pure CO_2 as working fluid with benefits for safety-of-operation, simultaneous generation of heat and cold, possibly co-generation of electricity or requiring limited input of electrical energy, thus providing a very high COP , exceeding, depending on the configuration, a COP of 3-5.

[0032] Example: A heat source supplies 1000 kW thermal energy, the heating medium is cooled from 70 to about 40° C. 1 kg CO₂ per second is liberated in the desorber from an absorbent system comprising amines as dislosed previously. Compression of 1 kg CO₂/s from 2 to about 20 bar requires 100 kW energy and generates roughly 100 kW thermal energy, e.g. in the form of a steam flow at 150° C. through outlet 6. This heat may be used in a paper mill for drying purposes or any other need including power generation. Cooling of CO₂ leads to a pressure decrease. CO₂ is further decompressed using e.g. a turbine generating (order of magnitude) 100 kW and is cooled. Cold is extracted, about 30 kW of cold (at -15 or -20° C.) can be extracted at heat exchanger 9. During the absorption of CO₂ by amine in 12, an equilibrium temperature of about 25-40° C. is reached, this heat may be partly removed by heat exchanging. Roughly 900 kW (thermal) are removed from the system by cooling, through cooling of the absorber 12 or cooling of lean, hot amine prior to transport into the absorber. With typically required pumping energies for absorbent in the order of 10-20 kW, a COP of (produced thermal energy) divided by (electrical power input)=130 kW/20=6.5 or higher is achieved.

[0033] Referring now to FIG. 2, a different embodiment is disclosed. A working fluid such as a ketone (acetone, MEK), an alcohol (methanol, ethanol, isopropanol), a paraffin (such as pentane), ammonia or amines, alone or in combination with water or water alone is pumped by pump (13) to the hot side of the process where at least part of the working fluid is evaporated in desorber (1), powered by thermal energy input (2) and (3). Some working fluid may be recycled for practical reasons (not shown). The working fluid enters compressor (4), is heat exchanged (5) and enters turbine (8) whereupon working fluid condenses in absorber (9). Condensed working fluid may be recycled to absorber (9) using pump (18) and cooler (16), however, main pump (13) may be used for that purpose in a modified scheme. Preferably, working fluid is sprayed into absorber (9) for efficiency and reduction of volume. A suitable system for concentration and ejection of non-condensable gas such as air is described in a separate disclosure (SE 100349-5) (see above).

[0034] In order to extract cold from expanding working fluid, it is preferred to use working fluids such as CO_2 and/or ammonia. Substantial heat extraction at (6) can pre-cool the working fluid. Condensable parts of the working fluid may be collected prior to turbine entry (8). These features which are obvious to persons skilled in the art are omitted in the drawings.

[0035] The common feature of embodiments 1 and 2 is that both systems operate partly below atmospheric pressure.

[0036] Both embodiments as in FIGS. 1 and 2 are useful in combination with district heating systems. Once the hot stream supplying heat to houses has cooled down from e.g. 80° C. to 50 or 40° C., this stream can be heated using the heat pump according to the invention. The advantages are that smaller pipes may be used for supplying district heat, as the same flow is used to supply more heat, in addition the return flow to the heat production unit can be lower in temperature,

compared to operation without the heat pump. This may increase the efficiency of heat generation or in some cases simultaneous electricity generation.

[0037] In the figures the reference characters used denote the following.

[0038] FIG. 1:

[0039] 1 Heat exchanger, waste heat input, rich absorbent mix desorbs CO₂;

[0040] 2 and 3 inflow heat, outflow heat source;

[0041] 4 compressor, compresses and heats CO₂ gas desorbed at 1:

[0042] 5 heat exchanger for extraction of high temperature;

[0043] 6 and 7 heat exchanger medium, e.g. liquid or steam;

[0044] 8 decompression, e.g. expansion machine, preferably coupled to 4, e.g. on same axis;

[0045] 9 (and 10/11) heat exchanger for extraction of low temperatures after expansion of gas;

[0046] 12 absorber, e.g. spray chamber with coupled heat exchanger (through 15/16);

[0047] 13 pump, for transport of CO₂ loaded absorbent mix to 1, 14 pipe to desorber heat exchanger 1;

[0048] 17 pipe for transport of CO₂-lean absorbent mix to absorber 12;

[0049] 18 pump for transport of lean absorbent to absorber, preferably coupled to 13;

[0050] 19 heat exchanger, for transfer of heat from lean to rich absorbent.

[0051] FIG. 2:

[0052] 1 Heat exchanger, waste heat input, working fluid evaporation;

[0053] 2 and 3 inflow heat, outflow heat source;

[0054] 4 compressor, compresses and heats gaseous working fluid desorbed at 1;

[0055] 5 heat exchanger for extraction of high temperature;

[0056] 6 and 7 heat exchanger medium, e.g. liquid or steam;

[0057] 8 decompression, e.g. expansion machine, preferably coupled to 4, e.g. on same axis;

[0058] 9 (and 10/11) heat exchanger for extraction of low temperatures after expansion of gas;

[0059] 12 supply line for condensed liquid from condenser (9) to pump (13);

[0060] 13 pump, for transport of working fluid to 1;

[0061] 14 pipe to desorber heat exchanger 1;

[0062] 18 pump for transport or recycling of working fluid to absorber, optionally coupled to 13;

1. A method for generation of energy where a heat source supplies thermal energy in the range 30-80° C. to a Rankine cycle including a desorber on the hot side, an absorber or liquefier on the cold side, heat exchangers and at least one compressor and at least one pump for working fluid, and at least one of the following product streams is obtained:

thermal energy in the range +90, +100, +120 and maximum $+200^{\circ}$ C..

thermal energy in the range +15, +10, +5, 0, -5 and minimum -20° C.,

electricity from the decompression of ${\rm CO}_2$ or a working fluid following the extraction of heat,

wherein the pressure in the absorber or condenser section are always below 1 bar and that the pressures and temperatures in the process are in the following specified ranges: Desorber: 0.5-5 bar, 30-80 $^{\circ}$ C.

Heat exchanger for heat production: 5-50 bar, 100-250° C., Absorber: 0.01-0.9 bar, 10-50° C.

- 2. The method according to claim 1 for co-generation of heat and cold and optionally electrical energy, using a heat source such as geothermal heat or waste heat in the range 30-80° C., comprising the following steps in an essentially closed loop:
 - a) condensing and cooling a working fluid such as acetone, ethanol, methanol, isopropanol, ammonia, or water, alone or in any stoichiometric combination, on the cold side of the process (absorber),
 - b) pumping said working fluid to the hot side of the process,
 - c) evaporating said working fluid using said geothermal or other waste heat source and compressing said working fluid from 0.5-5 bar to above 5 bar, or above 10 bar, preferably higher up to 50 bar,
 - d) extracting heat from said compressed working fluid and sending said heat to a point-of-use,
 - e) decompressing said working fluid whereupon cold is optionally extracted and sent to a different point-of-use,
 - f) condensing said working fluid (step a) for the cycle to start again.
- 3. The method according to claim 1 for co-generation of heat and cold and optionally electrical energy, using a heat source such as geothermal heat or waste heat in the range 30-80° C., comprising the following steps in an essentially closed loop system:
 - a) temporarily absorbing CO₂ as working fluid in a suitable absorbent comprising an alkaline medium such as at least one amine,
 - b) desorbing CO₂ from the absorbent using said geothermal or other waste heat source and compressing CO₂ from 0.3-3 bar to above 5 bar, or above 10 bar, preferably higher.
 - c) extracting heat from said compressed CO₂ and sending heat to a point-of-use,
 - d) decompressing CO₂ whereupon cold is optionally extracted and sent to a different point-of-use,
 - e) re-absorbing CO₂ in said absorbent system, for the cycle to start again.
- **4**. The method according to claim **1**, whereby a separate device is concentrating and ejecting non-condensable gas such as air from the process which at least partly operates below atmospheric pressure.
- 5. The method according to claim 1, where more electricity or work is consumed in the compression stage than is generated during the decompression.
- **6**. The method according to claim **1**, where the energy consumption of the method is reduced by coupling the gas compression for heat generation with the gas decompression, by mechanical, electrical or other means.
- 7. The method according to claim 1, in which a heat pump or heat transformer is realized within the technical boundaries of above mentioned claims.
- **8**. Use of the method according to claim **1**, in combination with a district heating system for elevating the temperature of the district heating medium or for electricity production on demand.

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