(19) DANMARK

(10) DK/EP 3077080 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *B 01 D 53/04 (2006.01)* *A 01 G 9/18 (2006.01)* *B 01 D 53/62 (2006.01)*
B 01 D 53/96 (2006.01) *B 01 J 20/04 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2019-05-20**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2019-02-20**

(86) Europæisk ansøgning nr.: **14809357.8**

(86) Europæisk indleveringsdag: **2014-12-03**

(87) Den europæiske ansøgnings publiceringsdag: **2016-10-12**

(86) International ansøgning nr.: **EP2014076462**

(87) Internationalt publikationsnr.: **WO2015082567**

(30) Prioritet: **2013-12-03 US 201361910977 P**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **CARBONDIOXIDBERIGELSESPROCES MED FUGTUDSVING**

(56) Fremdragne publikationer:
EP-A2- 1 074 297
EP-A2- 2 638 953
US-A1- 2013 004 394
US-A1- 2013 142 718
US-B1- 6 387 337

DESCRIPTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates generally to an absorption/desorption process for increasing the carbon dioxide concentration of a carbon dioxide-containing gas, and more specifically to an absorption/desorption process comprising a moisture swing.

2. Description of the Related Art

[0002] Our co-pending patent application WO2014/012966 describes a temperature swing process for producing a gas having relatively high carbon dioxide concentration. The process comprises heating of large volumes of gas, which requires significant amounts of energy.

[0003] Thus, there is a need for an improved swing absorption/desorption process for producing carbon dioxide rich gases.

BRIEF SUMMARY OF THE INVENTION

[0004] The present invention addresses these problems by providing a process for reversibly absorbing CO_2 to an alkali or earth alkaline metal absorbent, said process comprising a CO_2 absorption step wherein the alkali or earth alkaline metal absorbent is contacted with a first gas composition; and a CO_2 desorption step wherein the alkali or earth alkaline metal absorbent is contacted with a second gas composition, and the respective moisture contents of the first and second gas compositions are controlled such that during the absorption step the alkali or earth alkaline metal absorbent is converted to a bicarbonate, and during the desorption step the alkali or earth alkaline metal absorbent is converted to a carbonate hydrate, wherein the first gas composition is ambient air having a water vapor pressure of between 0.001 bar and 0.0150 bar, the first gas composition has a temperature of from -23.15 °C (250K) to 26.85 °C (300K), wherein the second gas composition has a water vapor pressure from 0.020 bar to 0.2 bar, the second gas composition has a temperature form 26.85 °C (300K) to 126.85 °C (400K), and the first composition is ambient air, optionally dried.

[0005] The process is particularly suitable for providing carbon dioxide to a greenhouse, to promote plant growth.

BRIEF DESCRIPTION OF THE FIGURES

[0006]

Figure 1 is a schematic representation of an apparatus for carrying out the process of the invention.

Figure 2 is a graphical representation of the carbon dioxide concentration of ambient air as a function of time.

Figure 3 represents the average carbon dioxide concentration of ambient air as measured in Figure 2.

Figure 4 is a graphic representation of the temperature of the air flow through the reactor of Figure 1.

Figure 5 is a graphic representation of the water vapor pressure of the air flow through the reactor of Figure 1.

Figure 6 is a graphic representation of the carbon dioxide concentration of the air flow.

Figure 7 is a schematic representation of an alternate embodiment of the apparatus for carrying out the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The following is a detailed description of the invention.

Definitions

[0008] The term "sesquihydrate" as used herein means a salt, such as a carbonate, having 1.5 mole of crystal water per mole of salt.

[0009] In its broadest aspect the present invention relates to process for reversibly absorbing CO_2 to an alkali or earth alkaline metal absorbent said process comprising a CO_2 absorption step wherein the alkali or earth alkaline metal absorbent is contacted with a first gas composition; and a CO_2 desorption step wherein the alkali or earth alkaline metal absorbent is contacted with a second gas composition, and the respective moisture contents of the first and second gas compositions are controlled such that during the absorption step the alkali or earth alkaline metal absorbent is converted to a bicarbonate, and during the desorption step the

alkali or earth alkaline metal absorbent is converted to a carbonate hydrate, wherein the first gas composition is ambient air having a water vapor pressure of between 0.001 bar and 0.0150 bar, the first gas composition has a temperature of from -23.15 °C (250K) to 26.85 °C (300K), wherein the second gas composition has a water vapor pressure from 0.020 bar to 0.2 bar, the second gas composition has a temperature form 26.85 °C (300K) to 126.85 °C (400K), and the first composition is ambient air, optionally dried

[0010] The absorbent can be any alkali metal or alkaline earth metal carbonate, in particular sodium carbonate or potassium carbonate, potassium carbonate being particularly preferred. The invention will be described in more detail with reference to potassium carbonate as the absorbent, but it will be understood that the invention is not limited in any way to the use of this absorbent.

[0011] The absorption reaction can be written as:

$$K_2CO_3+CO_2+H_2O \rightarrow 2KHCO_3 \qquad (1)$$

and the desorption reaction as:

$$2KHCO_3 \rightarrow K_2CO_3+CO_2+H_2O \qquad (2)$$

[0012] Absorption reaction (1) is exothermic (ΔH = - 141 kJ/mole), while desorption reaction (2) is endothermic (ΔH = + 141 kJ/mole). Two observations can be made. Firstly, the desorption reaction requires a large energy input. Secondly, the absorption step is favored by the presence of moisture, whereas the desorption step is favored by using a flush gas that is as dry as possible.

[0013] Studies by Duan et al. (see Duan, Y. et.al. (2012). Ab Initio Thermodynamic Study of the CO2 Capture Properties of Potassium Carbonate Sesquihydrate K2CO3•1.5H2O. The Journal of Physical Chemistry, 14461-14470) suggest a pathway through an intermediate species, namely potassium carbonate sesquihydrate, $K_2CO_3 \cdot 1.5H_2O$. Thus, reaction (1) can be written as two consecutive reactions:

$$K_2CO_3+1.5H_2O \rightarrow K_2CO_3 \cdot 1.5H_2O \qquad (1a)$$

$$K_2CO_3 \cdot 1.5H_2O+CO_2 \rightarrow 2KHCO_3+0.5H_2O \qquad (1b)$$

[0014] Reaction (2) can be written as:

$$2KHCO_3+0.5H_2O \rightarrow K_2CO_3 \cdot 1.5H_2O+CO_2 \quad (2a)$$

$$K_2CO_3 \cdot 1.5H_2O \rightarrow K_2CO_3+1.5H_2O \quad (2b)$$

[0015] Reactions (1a) and (1b) are exothermic (ΔH = -100 kJ/mole and -40 kJ/mole, respectively). The converse reactions are of course endothermic, ΔH being + 40 kJ/mole for reaction (2a) and +100 kJ/mole for reaction (2b).

[0016] EP2638953 relates to a method for recovering carbon dioxide from gases, in particular from process and combustion exhaust gases, wherein carbon dioxide-containing gas is passed over a porous support material which is loaded with a solution of at least one alkali carbonate to bind the carbon dioxide and wherein that carbon dioxide is released again by thermal decomposition of the compounds at high temperatures above the "decomposition" temperature of 120°C to form sodium carbonate.

[0017] It has now been discovered that an adsorption/desorption swing process can be operated such that the carbonate hydrate is the starting point of the absorption reaction, instead of being a reaction intermediary. Put differently, the absorption/desorption swing process uses the reaction pair (1b)/(2a), instead of reaction pair (1)/(2). This is accomplished by controlling the moisture contents of the absorption gas and the desorption gas.

[0018] Several observations need to be made. Firstly, the absorption reaction (1b) produces water, and is therefore favored by using an absorption gas having relatively low moisture content. Secondly, the desorption reaction (2a) consumes water, and is therefore favored by using a desorption gas that has relatively high moisture content. Thirdly, the reaction heat for desorption reaction (2a) requires an energy input of 40 kJ/mole, compared to 141 kJ/mole for reaction (2).

[0019] The process of the invention is particularly suitable for absorbing carbon dioxide from ambient air. The absorbing gas has a water vapor pressure of between 0.001 bar and 0.0150 bar, with water vapor pressures in the low end of this range being preferred. It may be desirable to subject the absorbing gas to a drying step, for example by passing a flow of the absorbing gas through a bed of a desiccant or a dry zeolite. In many cases the extra energy cost of the drying step is more than offset by greater absorption efficiency.

[0020] During the desorption step care must be taken not to remove crystal water from the carbonate material. Put differently, reaction (2b) must be avoided. For this reason the desorbing gas has a water vapor pressure from 0.020 bar to 0.2 bar. As the first, or absorbing, gas and the second, or desorbing, gas have different moisture contents, the process can be referred to as a moisture swing absorption/desorption process.

[0021] The moisture swing is combined with a modest temperature swing. The temperature of

the first gas is in the range of from 250K to 300K, and the temperature of the second gas is in the range of from 300K to 400K.

[0022] The first gas composition is ambient air, which is optionally dried, and preferably the second gas composition is obtained from a greenhouse, or ambient air that has been heated and moisturized. Generally, the atmosphere in a greenhouse is relatively humid, which makes it particularly suitable for use as the desorbing gas. Optionally additional moisture may be added to this gas before its use as the desorbing gas. The gas composition obtained from the greenhouse may optionally be heated prior to contacting the absorbent.

[0023] Likewise, ambient air may optionally be dried prior to contacting the absorbent in the absorption step. The air may also be subjected to a cooling step.

[0024] In this embodiment the second gas composition, after having been contacted with the absorbent, is enriched with carbon dioxide. This carbon dioxide-enriched gas composition is particularly suitable for plant growth (warm, humid air enriched in CO_2). It may be piped into the greenhouse to accelerate plant growth.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS/EXAMPLES

[0025] The following is a description of certain embodiments of the invention, given by way of example only.

[0026] Figure 1 shows a system for carrying out CO_2 capture from air at low temperatures through Relative Humidity Swing. The system was provided with two three-way valves. The positions of the valves during adsorption are shown in yellow. The positions of the valves during desorption are shown in blue.

[0027] The sorbent was formed by $K_2CO_3 \cdot 1.5H_2O$ supported on the surface of an Active Carbon (AC) honeycomb element, which acted as a thermodynamic carrier. No external heating was provided during the whole CO_2 capture/release cycle.

Preparation of the element.

[0028] Dimensions of the honeycomb monolith: 10*5*5cm. The AC honeycomb monolith was immersed in a 2:1 (mass ratio) K_2CO_3 solution during approximately 2 seconds. Then the element was dried in a furnace for 8 hours at 100°C in air. After this treatment the monolith's surface was loaded with a mixture of K_2CO_3 and $K_2CO_3 \cdot 1.5H_2O$ salts, which act as CO_2 captors according to the chemical reactions (1) and (1b) above.

[0029] The water adsorption of AC occurs parallel to these processes. The ΔH of the water

adsorption reaction can be approximated as the negative of the heat of vaporization of water:

$$H_2O_{(vap)} \rightarrow H_2O_{(ads)} \quad \Delta H = -45 \text{ KJ/mol at } 25°C \qquad [3]$$

[0030] Initially the reactor was fed with outside air (without any treatment) so CO_2 adsorption occurred via carbonation of the two salts, leading to the formation of $KHCO_3$. In the next stage the feeding air (untreated outside air) was pre-humidified by circulating it through a water flask, increasing its water vapor content. The humidified air was fed to the reactor, so the $KHCO_3$ decomposition (via reaction 2a) occurred. The 40.67 KJ/mol energy requirement was supplied by the adsorption of water vapor in the AC structure (reaction [3]). Experiments.

[0031] CO_2 background level.

[0032] CO_2 concentration in air was measured for two days. The results are shown in Figure 2. The average CO_2 concentration in air was 406 ppm (see Figure 3).

[0033] Experimental conditions.

[0034] The CO_2 adsorption was performed during night time when the T of the outside air is lower than during the day. Desorption of CO_2 was performed during day time. Air flow at the reactor inlet was 6.667 liters per minute; air flow at the reactor outlet was 6.333 liter per minute.

[0035] Table 1 shows the amount of salt present on the AC monolith. The molecular weight of dry potassium carbonate is 138.18; the molecular weight of the sesquihydrate is 165.18. For the calculation it was assumed that after the first adsorption/desorption cycle all salt was present as the sesquihydrate.

Table 1

SALT	PM (G/MOL)	N LOADED (MOL)	N CO_2 ADS (MOL)	M CO_2 (G)
DRY	138.18	0.086047	0.086047	3.786076
SESQUI	165.18	0.071982	0.071982	3.167212

[0036] The behavior of the temperature T of the air fed to and inside the reactor are plotted in Figure 4. T in the reactor is lower than the air fed during the adsorption mode because of the endothermic character of the process (water desorption from AC). In the CO2 desorption mode, the T of the reactor is higher than the air stream due to the exothermic character of the process (water adsorption onto AC). The T of the air stream varies from adsorption to

desorption modes because of the bypassing of the loop during CO2 desorption mode, i.e. the heat provided by the pump is not transferred (see figure 1).

[0037] Figure 5 shows the water vapor content of the air fed to the reactor and obtained from the reactor during the cycles. The inlet and outlet lines represent the P_{H2O} in the air stream at the inlet and outlet of the reactor, with the proviso that the water vapor pressure for the inlet during desorption was measured upstream of the humidifier. The Saturation line represents the saturation water vapor pressure, which is the expected value at the inlet during desorption modes as the air stream is bubbling through the water reservoir (humidifier), reaching a 100% RH.

[0038] Figure 6 shows the CO_2 adsorption-desorption cycles plotting [CO_2] in ppm (mol/mol) at the outlet of the reactor and P_{H2O} [bar], also at the outlet of the reactor, vs time [h]. The red horizontal line represents the average [CO_2] background value of 406 ppm.

[0039] Figure 7 shows an alternate embodiment of the present invention. In this embodiment the sorbent is a granulated, pelleted or powdered porous carrier with deposited thereupon the CO_2 adsorbing salt, referred to as the adsorbing material. Figure 7 shows an adsorption/desorption system 70. The adsorbing material is circulated continuously from adsorption zone 71, via a de-aeration zone 72, to a desorption zone 73. In adsorber 71 the adsorbent is contacted with the gas from which CO_2 is to be adsorbed. This can be air, optionally dried and cooled to aid CO_2 adsorption, or flue gas, optionally dried and cooled, or any other gas stream containing CO_2. Alternatively, the sorbent material can be mixed with a mild desiccant or a dry zeolite to shift the equilibrium, during adsorption to lower final CO_2 concentrations in the contacting gas by simultaneously adsorbing the moisture released during adsorption via reaction 1b.

[0040] In de-aerator 72, the gas from which CO_2 was to be adsorbed that is entrained with the saturated adsorbent is displaced with a gas that is more suitable for the downstream process. For some applications, oxygen in the downstream gas may be undesirable, (such as CCS (Carbon Capture and Storage and CCU (Carbon Capture and Utilization)), and the sorbent may be de-aerated with, for example, nitrogen. For other applications, such as greenhouses, the de-aeration step may be omitted.

[0041] In desorber 73 the sorbent is contacted with a heated gas, optionally with added moisture to aid desorption. In the desorber, the sorbent is regenerated via reaction 2a, and, if present, the desiccant or zeolite is also regenerated. The moisture released by the regeneration of the desiccant or zeolite helps shift reaction 2a to further desorb CO_2. The heat supplied for desorption is indicated as input flows 74 and 75. The adsorption temperature T1 in adsorber 71 is lower than desorption temperature T2 in desorber 73. For example, T1 may be in the range from 250K to 300K and temperature T2 may be in the range from 300K to 400K.

[0042] In the example of figure 7, the nitrogen that is used as a heat carrier and a carrier gas to move CO_2 from the sorbent during the desorption is recycled, and CO_2 is separated from this gas by utilizing their different saturation pressures, and liquefying the CO_2 out of the carrier gas stream by compression. The energy spent for compression of the carrier gas is then (partly) recovered, the condensation heat of the CO_2 may also be (partly) utilized as heat source for the desorption step. This mode of operation is particularly suitable for CCS and CCU applications.

[0043] Thus, the invention has been described by reference to certain embodiments discussed above. It will be recognized that these embodiments are susceptible to various modifications and alternative forms well known to those of skill in the art.

[0044] Many modifications in addition to those described above may be made to the structures and techniques described herein without departing from the scope of the invention. Accordingly, although specific embodiments have been described, these are examples only and are not limiting upon the scope of the invention.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO2014012966A [0002]
- EP2638953A [0016]

Non-patent literature cited in the description

- **DUAN, Y.**Ab Initio Thermodynamic Study of the CO2 Capture Properties of Potassium Carbonate Sesquihydrate K2CO3•1.5H2OThe Journal of Physical Chemistry, 2012, 14461-14470 [0013]

P A T E N T K R A V

1. Fremgangsmåde til reversibelt at absorbere CO_2 til en alkali- eller jordalkalimetalabsorbant, hvilken fremgangsmåde omfatter et CO_2-absorptionstrin, hvori alkali- eller jordalkalimetalabsorbanten bringes i kontakt med en første gassammensætning;
og et CO_2-desorptionstrin, hvori alkali- eller jordalkalimetalabsorbanten bringes i kontakt med en anden gassammensætning, og det respektive fugtindhold i den første og anden gassammensætning styres, således at alkali- eller jordalkalimetalabsorbanten under absorptionstrinnet omdannes til et bicarbonat, og alkali- eller jordalkalimetalabsorbanten under desorptionstrinnet omdannes til et carbonathydrat, hvor den første gassammensætning eventuelt tørres, hvor den omgivende luft har et vanddamptryk på mellem 0,001 bar og 0,0150 bar og har en temperatur på fra -23,15 °C (250 K) til 26,85 °C (300 K), hvor den anden gassammensætning har et vanddamptryk fra 0,020 bar til 0,2 bar og har en temperatur fra 26,85 °C (300 K) til 126,85 °C (400 K).

2. Fremgangsmåde ifølge krav 1, hvori absorbanten er en natrium- eller kaliumabsorbant.

3. Fremgangsmåde ifølge krav 2, hvori absorbanten er en kaliumabsorbant.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori carbonathydratet er kaliumcarbonat-sesquihydrat.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori den anden gassammensætning er opnået fra et drivhus.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori den anden gassammensætning opvarmes, før den bringes i kontakt med absorbanten.

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori der tilsættes fugt til den anden gassammensætning, før den bringes i kontakt med absorbanten.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori den første gassammensætning udsættes for nedkøling, før den bringes i kontakt med absorbanten.

9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvori den første gassammensætning bringes i kontakt med et tørremiddel, før den bringes i kontakt med absorbanten, og tørremidlet med mellemrum udsættes for regenerering.

DRAWINGS

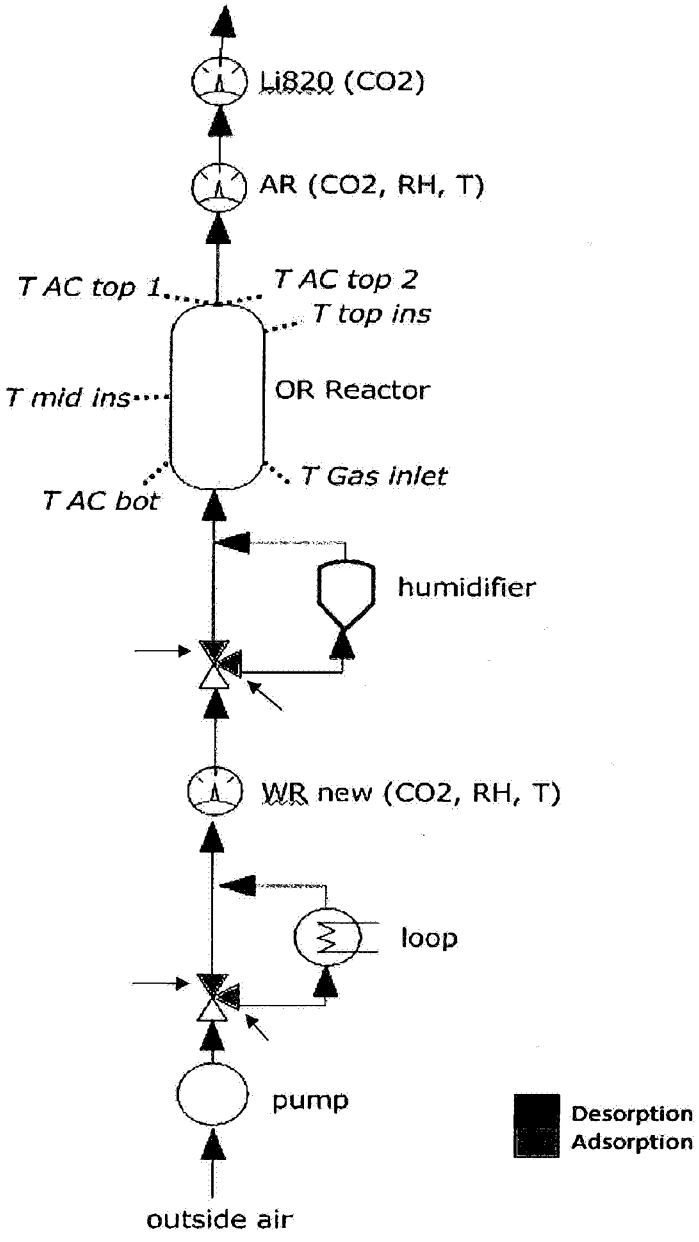


Figure 1

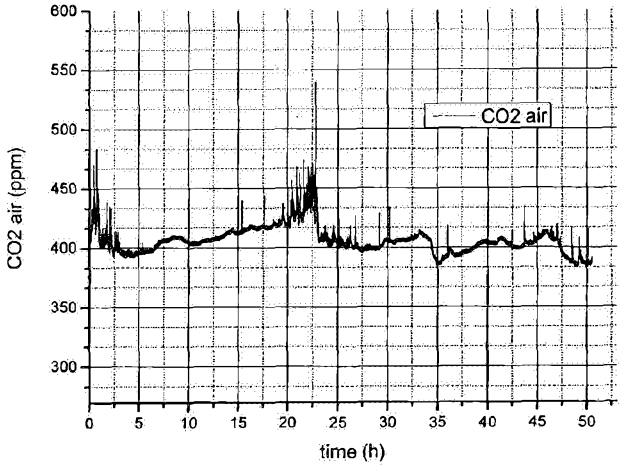


Figure 2

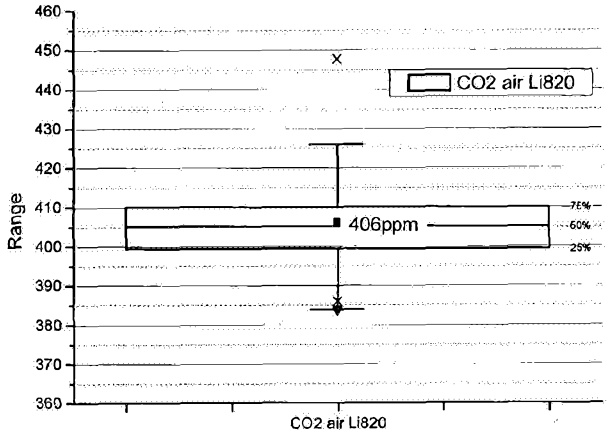


Figure 3

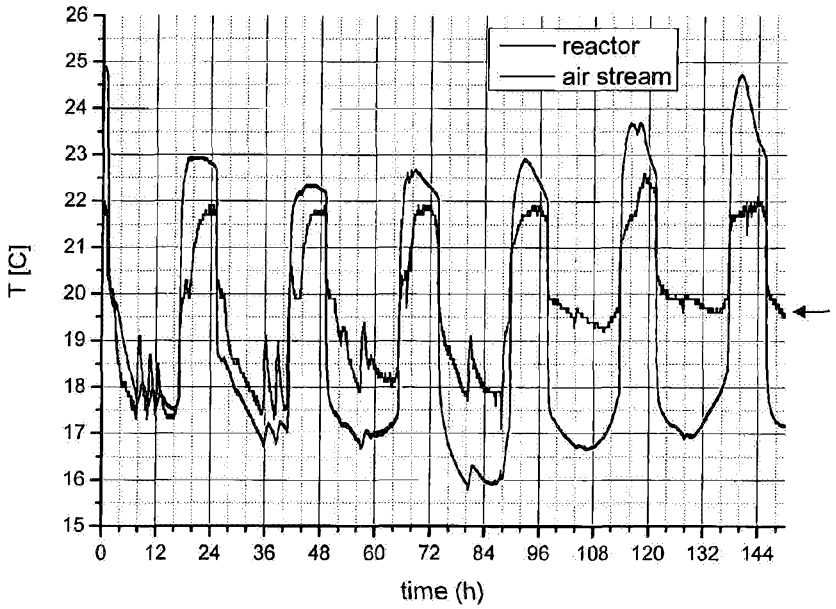

reactor
air stream
T [C]
time (h)
26
25
24
23
22
21
20
19
18
17
16
15
0
12
24
36
48
60
72
84
96
108
120
132
144

Figure 4

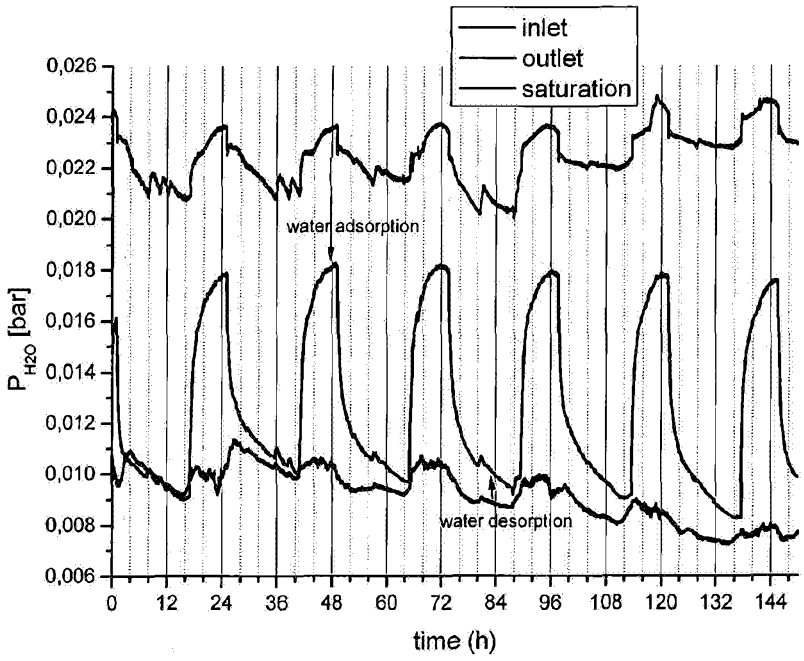

inlet
outlet
saturation
water adsorption
water desorption
P_{H2O} [bar]
0,026
0,024
0,022
0,020
0,018
0,016
0,014
0,012
0,010
0,008
0,006
0
12
24
36
48
60
72
84
96
108
120
132
144
time (h)

Figure 5

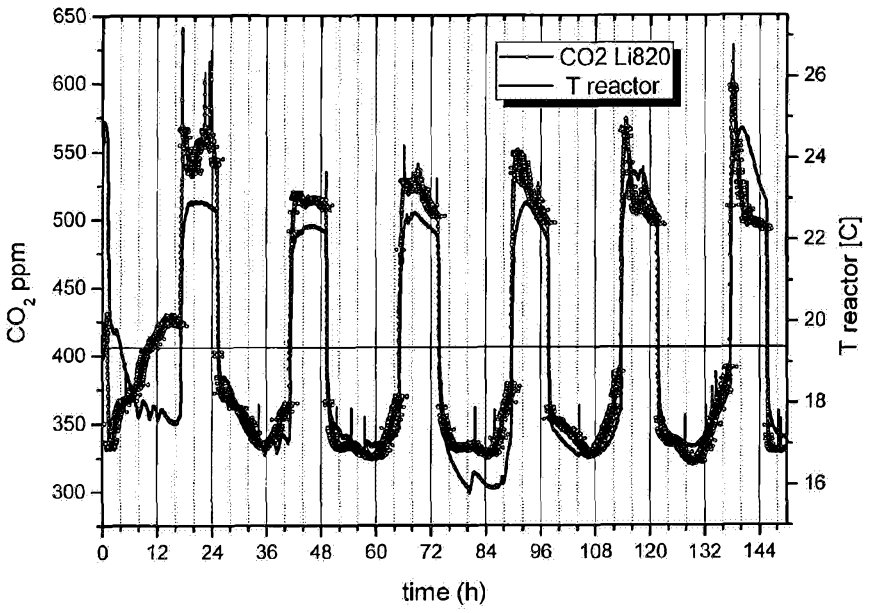

CO2 Li820
T reactor
CO_2 ppm
T reactor [C]
time (h)
650
600
550
500
450
400
350
300
26
24
22
20
18
16
0
12
24
36
48
60
72
84
96
108
120
132
144

Figure 6

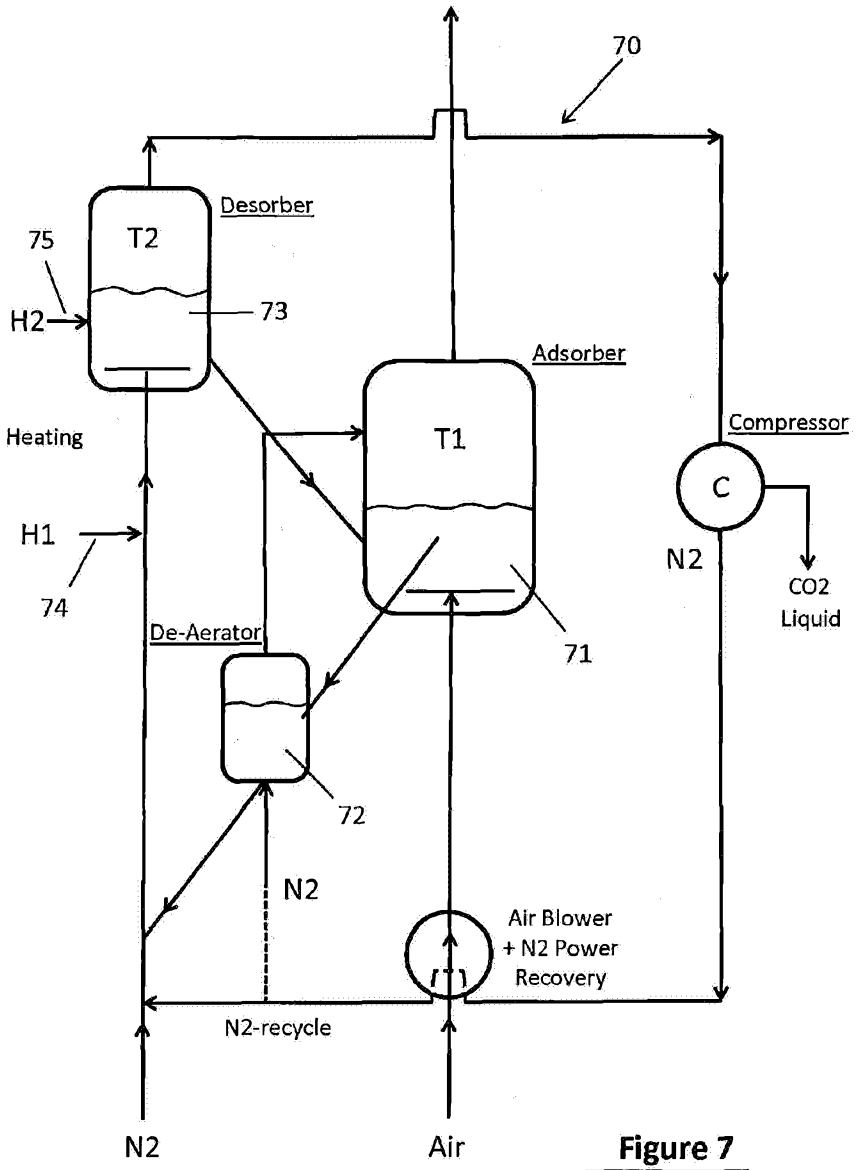

70
Desorber
T2
75
H2
73
Adsorber
T1
Compressor
C
N2
CO2
Liquid
Heating
H1
74
De-Aerator
71
72
N2
Air Blower
+ N2 Power
Recovery
N2-recycle
N2
Air

Figure 7