

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro



(43) Internationales Veröffentlichungsdatum
23. September 2010 (23.09.2010)

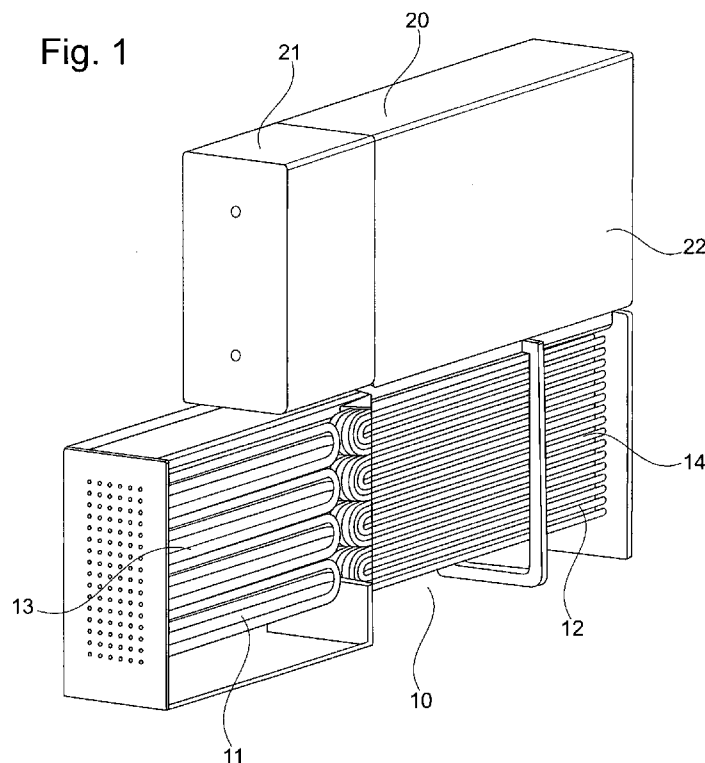
(10) Internationale Veröffentlichungsnummer
WO 2010/105613 A3

- (51) Internationale Patentklassifikation: *F28D 7/00* (2006.01) *F28D 7/06* (2006.01) Strasse 27, 10997 Berlin (DE). **JAHNKE, Anna** [DE/DE]; Bergmannstrasse 91, 10961 Berlin (DE).
- (21) Internationales Aktenzeichen: PCT/DE2010/000309 (74) **Anwalt: BOEHMERT & BOEHMERT**; Hollerallee 32, 28209 Bremen (DE).
- (22) Internationales Anmeldedatum: 19. März 2010 (19.03.2010) (81) **Bestimmungsstaaten** (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (25) Einreichungssprache: Deutsch
- (26) Veröffentlichungssprache: Deutsch
- (30) Angaben zur Priorität: 10 2009 013 684.3 20. März 2009 (20.03.2009) DE
- (71) **Anmelder** (für alle Bestimmungsstaaten mit Ausnahme von US): **TECHNISCHE UNIVERSITÄT BERLIN** [DE/DE]; Strasse des 17. Juni 135, 10623 Berlin (DE).
- (72) **Erfinder; und**
- (75) **Erfinder/Anmelder** (nur für US): **PETERSEN, Stefan** [DE/DE]; Seumestrasse 30, 10245 Berlin (DE). **FINCK, Christian** [DE/DE]; Senffstrasse 22, 06120 Halle/Saale (DE). **MITTERMEIER, Martin** [DE/DE]; Lübbener
- (84) **Bestimmungsstaaten** (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE,

[Fortsetzung auf der nächsten Seite]

(54) Title: HEAT EXCHANGER UNIT AND THERMOTECNICAL SYSTEM

(54) Bezeichnung : WÄRMETAUSCHEREINHEIT UND WÄRMETECHNISCHE ANLAGE



(57) **Abstract:** The invention relates to a heat exchanger unit having an evaporator device configured for evaporating a heat exchanger operating fluid, and a condenser device configured for condensing the heat exchanger operating fluid, wherein the evaporator device and the condenser device are fluidically connected to each other in a frontal configuration. The invention further relates to a thermotechnical system having a plurality of heat exchanger units.

(57) **Zusammenfassung:** Die Erfindung betrifft eine Wärmetauschereinheit mit einer Verdampferanordnung, die konfiguriert ist, ein Wärmetauscherbetriebsmittel zu verdampfen, und einer Verflüssigeranordnung, die konfiguriert ist, das Wärmetauscherbetriebsmittel zu verflüssigen, wobei die Verdampferanordnung und die Verflüssigeranordnung für ein Überströmen des Wärmetauscherbetriebsmittels in Fluidverbindung stehen und zueinander in einer stirnseitigen Konfiguration angeordnet sind. Weiterhin ist eine wärmetechnische Anlage mit mehreren Wärmetauschereinheiten geschaffen.

WO 2010/105613 A3



DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI,
SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

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Frist; Veröffentlichung wird wiederholt, falls Änderun-
gen eingehen (Regel 48 Absatz 2 Buchstabe h)

Veröffentlicht:

— mit internationalem Recherchenbericht (Artikel 21 Absatz
3)

**(88) Veröffentlichungsdatum des internationalen Recher-
chenberichts:**

10. März 2011

INTERNATIONAL SEARCH REPORT

International application No
PCT/DE2010/000309

A. CLASSIFICATION OF SUBJECT MATTER INV. F28D7/00 F28D7/06 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) F28D				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 5 845 703 A (NIR ARI [US]) 8 December 1998 (1998-12-08) figures 1,4 -----	1,2,6,7, 9		
X	US 3 817 708 A (VERNON W) 18 June 1974 (1974-06-18) figure 3 -----	1,2,6-8, 10		
X	GB 951 694 A (VORKAUF HEINRICH) 11 March 1964 (1964-03-11) figures 1-3 -----	1-7		
X	GB 2 451 848 A (ARCTIC CIRCLE LTD [GB]) 18 February 2009 (2009-02-18) figure 1 ----- -/--	1,2,6,7		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> See patent family annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.			
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family			
Date of the actual completion of the international search <p style="text-align: center; font-size: 1.2em;">13 December 2010</p>		Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">30/12/2010</p>		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <p style="text-align: center; font-size: 1.2em;">Vassoille, Bruno</p>		

INTERNATIONAL SEARCH REPORT

International application No
PCT/DE2010/000309

C(Continuation). . . DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 15 51 523 A1 (WILLY SCHELLER MASCHB KG FA) 19 March 1970 (1970-03-19) figure 2 -----	1,2,6,7
X	JP 2000 111212 A (SANYO ELECTRIC CO) 18 April 2000 (2000-04-18) figure 2 -----	1,2,6,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/DE2010/000309

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5845703	A	08-12-1998	AT 208878 T 15-11-2001
			AU 714864 B2 13-01-2000
			AU 2339397 A 01-10-1997
			CA 2239878 A1 18-09-1997
			DE 69708274 D1 20-12-2001
			EP 0890061 A1 13-01-1999
			JP 2000506593 T 30-05-2000
			WO 9734107 A1 18-09-1997
			US 5626102 A 06-05-1997
			US 5797447 A 25-08-1998
			US 5893411 A 13-04-1999
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US 3817708	A	18-06-1974	NONE
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GB 951694	A	11-03-1964	DE 1401713 A1 12-12-1968
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<hr style="border-top: 1px dashed black;"/>			
DE 1551523	A1	19-03-1970	NONE
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JP 2000111212	A	18-04-2000	NONE
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INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/DE2010/000309

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES INV. F28D7/00 F28D7/06 ADD.		
Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC		
B. RECHERCHIERTE GEBIETE		
Recherchiertes Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole) F28D		
Recherchierte, aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen		
Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe) EPO-Internal		
C. ALS WESENTLICH ANGESEHENE UNTERLAGEN		
Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	US 5 845 703 A (NIR ARI [US]) 8. Dezember 1998 (1998-12-08) Abbildungen 1,4 -----	1,2,6,7,9
X	US 3 817 708 A (VERNON W) 18. Juni 1974 (1974-06-18) Abbildung 3 -----	1,2,6-8,10
X	GB 951 694 A (VORKAUF HEINRICH) 11. März 1964 (1964-03-11) Abbildungen 1-3 -----	1-7
X	GB 2 451 848 A (ARCTIC CIRCLE LTD [GB]) 18. Februar 2009 (2009-02-18) Abbildung 1 ----- -/--	1,2,6,7
<input checked="" type="checkbox"/> Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen <input checked="" type="checkbox"/> Siehe Anhang Patentfamilie		
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Datum des Abschlusses der internationalen Recherche 13. Dezember 2010		Absendedatum des internationalen Recherchenberichts 30/12/2010
Name und Postanschrift der Internationalen Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Bevollmächtigter Bediensteter Vassoille, Bruno

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/DE2010/000309

C. (Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN		
Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	DE 15 51 523 A1 (WILLY SCHELLER MASCHB KG FA) 19. März 1970 (1970-03-19) Abbildung 2 -----	1,2,6,7
X	JP 2000 111212 A (SANYO ELECTRIC CO) 18. April 2000 (2000-04-18) Abbildung 2 -----	1,2,6,7

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/DE2010/000309

Im Recherchenbericht angeführtes Patentedokument		Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
US 5845703	A	08-12-1998	AT 208878 T	15-11-2001
			AU 714864 B2	13-01-2000
			AU 2339397 A	01-10-1997
			CA 2239878 A1	18-09-1997
			DE 69708274 D1	20-12-2001
			EP 0890061 A1	13-01-1999
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			WO 9734107 A1	18-09-1997
			US 5626102 A	06-05-1997
			US 5797447 A	25-08-1998
			US 5893411 A	13-04-1999

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GB 2451848	A	18-02-2009	KEINE	

DE 1551523	A1	19-03-1970	KEINE	

JP 2000111212	A	18-04-2000	KEINE	



- (51) **International Patent Classification:**
F28D 20/00 (2006.01) *F25B 17/08* (2006.01)
- (21) **International Application Number:**
PCT/NL2015/050604
- (22) **International Filing Date:**
1 September 2015 (01.09.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
14183276.6 2 September 2014 (02.09.2014) EP
- (71) **Applicant:** NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO [NL/NL]; Anna van Buerenplein 1, NL-2595 DA 's-Gravenhage (NL).
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- (74) **Agents:** JANSEN, C.M. et al.; V.O., Carnegieplein 5, 2517 KJ Den Haag (NL).

- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) **Title:** SYSTEM AND METHOD FOR THERMOCHEMICAL STORAGE OF ENERGY

(57) **Abstract:** The present invention discloses a closed system for thermochemical storage comprising at least one water condenser and at least two thermochemical modules, wherein a first thermochemical module comprises a first thermochemical material and a second thermochemical module comprises a second thermochemical material, and wherein the at least one water condenser and the thermochemical modules are connected so that water vapour can be exchanged individually between any two selected from the list consisting of the at least one water condenser and the at least two thermochemical modules. A method for desorption in the system according to the invention is also described. In this method, the first thermochemical module is used as a condenser to dry the second thermochemical module.



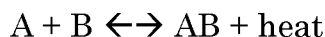
WO 2016/036242 A1

Title: System and method for thermochemical storage of energy

5 The invention relates to the area of seasonal heat storage and systems and materials useful therefor.

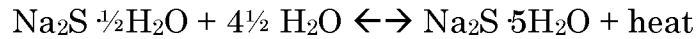
There is a growing interest for the use of thermal solar collectors to obtain energy that can be used for various needs in houses, and particularly for space heating and provision of hot water. As an estimation,
10 an area of 10-20 m² of solar panels would be sufficient for the annual heat demand of about 20 GJ of a good isolated dwelling, provided that the surplus could be used for the deficit in the winter. This requires storage of about 10 GJ. If this is stored in a hot water tank, this would need about 50 m³ (for a tank at 90°C), which would be too big for domestic applications. An
15 attractive alternative is to store heat by drying thermochemical materials (TCM) with an excess of solar heat from *e.g.* solar collectors in the summer. In the winter, it is then possible to hydrate the TCM and in this way to release the heat.

In general, thermochemical heat storage (TCS) is based on
20 thermally reversible reactions such as:



The reaction may contain more compounds and is not restricted to two compounds A and B. For the above reaction, the charging process to store the energy is an endothermic reaction wherein heat is supplied to split
25 compound AB into compounds A and B. The energy is released in the form of heat when A and B are brought together (discharging process). A can be referred to as a sorption material (or sorbent), B is a working fluid (or sorbate), AB is working fluid adsorbed (or absorbed) on the sorption material. A and B can also both be fluid.

These reaction are also called sorption and desorption reactions. In case of water being one of the compounds A or B, these are hydration or dehydration reactions, for example:



5 This sorption or hydration reaction provides for a high energy density of about 2.7 GJ per m³ of Na₂S · 5H₂O, whereby the heat for evaporation is supplied from an external source. TCM do not only have a higher heat storage compared to hot water storage, but also do not require thermal insulation. One only needs to keep chemical components separate,
10 in the above case dried sodium sulfide and water, which is ideal for seasonal storage.

There are however some problems in the use of TCM for thermochemical heat storage. For example, zeolite and silica, although being stable for many cycles of hydration and dehydration, they have a
15 relatively low storage density for drying at a typical solar collector temperature of 90°C (and for typical condenser, evaporator and sorption temperatures). With hygroscopic salts, higher storage densities to 1-2 GJ/m³ are possible but for these materials undesirable processes could play a role especially at higher temperatures, such as melting, coagulation, volume
20 changes during hydration or dehydration, scaling, corrosion, decomposition, and other undesirable chemical side reactions.

The present invention aims to provide a system and a method for thermochemical storage of heat having one or more of the following advantages: (1) high storage density at a given desorption temperature,
25 which is preferably with a factor higher than that of zeolite, (2) low desorption temperatures, so that the negative effects mentioned herein-above are reduced or disappear.

In order to address at least some of the above desires, the present invention provides, in one aspect, a closed system for thermochemical
30 storage comprising at least one water condenser and at least two

thermochemical modules, wherein a first thermochemical module comprises a first thermochemical material and a second thermochemical module comprises a second thermochemical material, and wherein the at least one water condenser and the thermochemical modules are connected so that
5 water vapour can be exchanged individually between any two selected from the list consisting of the at least one water condenser and the at least two thermochemical modules.

In another aspect, the present invention provides a method for desorption in a system for thermochemical storage according to the
10 invention, comprising a step wherein the desorption in the second thermochemical module is realized using at least the first thermochemical module as a condenser.

Under “condenser” throughout this specification and the claims a module is understood that is capable of generating and – in reverse –
15 accommodating water vapour. Condenser can for example be a water condenser, which contains liquid water as the source of the water vapour. However in certain use modes, a thermochemical module can be used as a condenser. Condenser can typically operate in two modes – (1) generating water vapour (evaporating mode) and (2) absorbing/accommodating of water
20 vapour (drying mode). Water condenser is typically provided with a heat source to control the temperature of the condenser.

A thermochemical (TCM) module is a module containing thermochemical material. A thermochemical module is typically provided with a heat source (heat exchanger), in order to control the temperature of
25 the module. Thermochemical materials are able to undergo reversible reactions wherein sorption of a certain compound is associated with heat release. Typical thermochemical materials are known to a skilled person and are for examples salts, hydrates releasing heat when reacting with water to form (higher) hydrates, as exemplified above. An overview of some
30 thermochemical materials is presented in P. Tatsidjodoung, N. Le Pierrès

and L. Luo, «A review of potential materials for thermal energy storage in building applications», *Renew. Sustain. Energy Rev.*, vol. 18, n. 0, p. 327-349, Feb. 2013. Generally, thermochemical materials can be divided into a group of sorption phenomena materials, *e.g.* zeolites, in which the sorbate is
5 physically adsorbed and/or absorbed by the material, and chemical reaction materials, *e.g.* oxides/hydroxides and hydrate-forming salts, wherein the sorbate is chemically bonded to the material. In the latter case the sorption leads to the formation of another chemical compound (hydroxide from a respective oxide) or the sorbate is included into the crystal structure of the
10 material, *e.g.* forming a hydrate. Particularly preferred in the present invention are the thermochemical materials that react with water (vapour) as the sorbate to release heat.

Prior art methods can be illustrated based on Figure 1A. In this figure a system is shown comprising a water condenser and one TCM
15 module, connected through a valve for water vapor with the water condenser. To charge the thermochemical storage, the thermochemical module is heated (*e.g.* heat from solar collectors) at a desorption temperature T_D to release a certain amount of water vapour. The vapor produced thereby is condensed in the water condenser at a condensation
20 temperature T_C and the associated waste heat is released. The condensed water and dehydrated sorbent are stored in separate tanks at ambient temperature. As long as these agents are not put in contact again, no heat losses occur.

For the heat release, the water stored in the water condenser is
25 vaporized at an evaporation temperature T_E using a heat source. The vapor is then absorbed by the dehydrated sorbent in the TCM module at a sorption temperature T_S releasing its enthalpy of absorption. The thereby generated heat is used, *e.g.* for space heating or domestic hot water production.

When water condenser is used to dry the TCM module as in
30 Figure 1A, and it is a water condenser at an ambient temperature, for

example 30°C in the summer, then the saturation vapor pressure of 42 mbar of water at 30°C is limiting for the whole process. This vapour pressure in fact determines how much heat can be stored. In most cases, this means that the TCM cannot be completely dried without increasing the temperature T_D . However, increasing the temperature T_D can be difficult or unpractical. For example, a typical desorption temperature that can be realized using solar collectors is 90°C. It is difficult to use a higher temperature when water is used as the heat exchange medium as the water will start to boil.

10 The present invention is based on a judicious insight that it is possible to use a lower desorption temperature by using an earlier dried TCM module instead of using a water condenser with a water surface. In this way, (1) TCM can be much further dried at a given temperature T_D , resulting in a much higher storage density or (2) TCM can be dried at a lower temperature T_D while maintaining the same energy storage density. The procedure can be extended to multiple stages of drying. If a collection of TCM modules is used, then the modules can dry each other in steps. There are several strategies for multistage drying possible, some of which will be explained in more details herein-below.

20 In the multistage thermochemical storage according to the invention, a TCM module is subjected to hydration/dehydration at the same temperature with another TCM module, instead of with the evaporator/condenser of water vapor. In this way, completely dry TCM, *e.g.* Z13X with water loading (B) nearly 0 is possible to achieve without increasing the temperature T_D , or even at a lower T_D . For the 2nd, 3rd and further stages, the TCM module can be used at T_C as a condenser.

30 In some embodiments, the thermochemical material used in the method of the present invention is selected from the group consisting of zeolites, silica gel, hygroscopic salts, metal-organic frameworks (MOF), carbon, and aluminum phosphates. In some preferred embodiments, the

thermochemical material is a sorption phenomenon material, such as zeolites, silica gel, MOF, carbon and aluminum phosphates. An advantage of such materials is that they typically do not swell/shrink during (de)sorption and therefore exhibit a rather good stability during recycling. A
5 disadvantage is however that sorption phenomenon materials usually have a rather low heat storage density. In other preferred embodiments, the thermochemical material used in the method is a chemical reaction material, *e.g.* hygroscopic salts. Salts possess a rather high heat storage density but the sorption/desorption processes are likely to disrupt the
10 crystal structure, which leads to a lower recycling stability. The hygroscopic salts are usually capable of forming hydrates. Preferably, the hygroscopic salt is selected from the list consisting of chlorides, sulfates, iodides, nitrates, sulfides and its hydrates. Examples are sodium sulfide, magnesium chloride and its hydrates. In some embodiments, it is preferred
15 to use thermochemical materials that allow multistage sorption/desorption, *e.g.* salts that form several hydrates. In some embodiments, the thermochemical material is in the solid form.

In some embodiments, the multiple thermochemical modules comprise the same thermochemical material. In other embodiments, the
20 modules may comprise different thermochemical materials. For example, one thermochemical module may comprise a sorption phenomenon material, and the other one a chemical reaction material. In one of the embodiments, the thermochemical module used as a condenser contains silica gel, while the other thermochemical module contains a hygroscopic salt. In another
25 embodiment, both TCM modules contain a hygroscopic salt.

Also the weight of the thermochemical material can be varied. In some embodiments, the thermochemical modules contain the same amount of the thermochemical material, while in other embodiments it can be advantageous to use more material in one of the TCM modules, *e.g.* in the
30 one which works as a condenser. This means that the TCM modules may

have the same or different volumes. In some embodiments, it is preferred to use identical TCM modules having the same volume and the same thermochemical material.

A system according to the invention with two stages (two
5 modules) is illustrated in Figure 1B. Instead of a water condenser another TCM module M_1 is used. The TCM modules are connected using a duct and a valve. In this embodiment, TCM module M_2 is subjected to hydration/dehydration at the same T_D with another TCM module M_1 , instead of with the evaporator/condenser of water vapor. For practical
10 purposes, the system should further comprise a water condenser (not shown) that can be used to dry the TCM module used as a condenser.

The system is not limited to two TCM modules; more than two TCM modules can be used. In some embodiments, three TCM modules are used. Also more than one water condenser can be used, which may be
15 advantageous in certain embodiments.

In a preferred embodiment, the at least one water condenser and the TCM modules are all connected in such a way that predetermined condensers and/or modules could be brought into contact independently of each other. Particularly, the connection is such as to allow individual
20 connections between any two modules, wherein the modules are selected from the list consisting of the at least one water condenser and the at least two thermochemical modules. In other words, the system according to the invention allows exclusive connections between the thermochemical modules (any combinations of two modules), but also between a TCM
25 module and a water condenser, and also between water condensers (in case there are more than one). Exclusive connection means that there is no water vapour transfer with the other modules/water condensers except between those forming the exclusive connection. These can be two modules, but also three or more.

The possibility of forming exclusive connections between any combinations of modules is an important characteristic of the system according to the present invention and makes it possible to realize the method for desorption/sorption according to the invention wherein one thermochemical module is dried using another thermochemical module. Exclusive connections allow a great flexibility and particularly, allow to use TCM modules in different roles. The same TCM module can be first hydrated using a water condenser but in another step the TCM module is used as a condenser itself, when connected to another TCM module. Similarly, the present system allows a connection in which one TCM module (or modules) operates in a sorption mode thereby adsorbing water vapour, while another TCM module (or modules) operates in a desorption mode thereby generating water vapour.

The above described property of exclusive connections can be realized by providing a connection system wherein each water condenser and each TCM module has a connection through a valve with a central tube. Such central tube can also have a ring (loop) form. The connection and the central tube allow the exchange of vapour between different modules. By selectively opening and closing the valves, different connections between the condenser(s) and TCM modules can be realized.

An example of such connection system is shown in Figure 9. The central tube can have different configurations, it may be linear as in Figure 9 but can also be in the form of a ring or loop. Use of a tube to connect different pieces of equipment is flexible in application as it allows different configurations to be realized. For example, it allows to connect and realize water vapour exchange between one selected TCM module and a water condenser, but also between two TCM modules, and even between three TCM modules. The latter case can be useful in an embodiment wherein two TCM modules are used to dry a third TCM module (described herein-below in more detail).

Initially, the central tube can be evacuated to a reduced pressure, more preferably vacuum. This can be done when all valves of the condenser(s) and TCM modules are closed. For example, this could be done when in between the steps of bringing into contact of selected condenser(s) and/or TCM modules by opening the respective valves. Bringing the central tube to vacuum (*e.g.* under 0.01 mbar) has an advantage that the vapour pressure equilibrium is set more precisely.

In an interesting embodiment, two TCM modules can be used simultaneously to dehydrate a third TCM module. This has as an advantage that higher dehydration degrees can be reached.

In a further aspect, the present invention provides a method for desorption in a system for thermochemical storage according to the invention, wherein the desorption in the first thermochemical module is realized using the second thermochemical module as a condenser, instead of a water condenser.

This method can be illustrated on the two module system depicted in Figure 1B. Both modules M_1 and M_2 are heated up to a certain temperature T_D , using a heating source. Then the valve is closed to prevent the exchange of water vapour between the modules. The left module, M_1 , is then cooled down to the temperature T_C (part of that energy can be collected in the heat exchanger). The right module M_2 still has the temperature T_D . In the next step, the valve is open and the water vapour can be exchanged. Because of a difference in water vapour pressure in the modules, a new water vapour pressure will be set, which is equal in both M_1 and M_2 . This will lead to the transport of an amount of water vapour from M_2 to M_1 . Effectively, the M_2 module will be dried and the M_1 module will accommodate the water vapour thus working as a condenser.

As will be illustrated in the examples, the advantage of this type of drying is that the same (lower) water loading B of the TCM in M_2 can be

achieved at a lower temperature T_D than if a water condenser was used instead of M_1 .

The possibility to use lower desorption temperatures mean more advantages. First of all, more types of TCM can be used, as some of these
5 materials tend to show instability at higher temperatures. Further, at lower collector temperatures (e.g. 70°C instead of 90°C) the heat loss of solar collectors to ambient is lower, and lower collector temperatures are reached more often, so that TCM can be dried more often.

The TCM modules typically comprise a heat exchanger that
10 allows to bring the module at a required temperature – for example T_D or T_C . The heat released in the TCM module used as a condenser (e.g. M_1 in Figure 1B), can be collected through a heat exchanger present in that module. Heat exchangers using concurrent flow allow to recover theoretically up to 50% of the released heat. If countercurrent flow is used,
15 theoretically up to 100% of the released heat can be collected.

Since the processes of sorption and desorption are interrelated, the present invention can equally be used as a method for sorption in a system for thermochemical storage according to the invention, wherein the sorption in the first thermochemical module is realized using the second
20 thermochemical module as an evaporator, instead of a water evaporator. The advantage of this is that higher sorption temperatures in the second thermochemical module can be realized.

In a separate embodiment of the present invention, the step of sorption using a thermochemical module as an evaporator can also be
25 realized through an intermediate water evaporator. Figure 10 illustrates such an embodiment. This embodiment includes the use of a cold water evaporator and a warm water evaporator and further of two TCM modules M_1 and M_2 . The role of the cold and warm water evaporators can also be fulfilled by the same evaporator. The embodiment can realize a higher

temperature of sorption (60°C instead of 40°C). An example of a method, wherein such configuration is used is discussed in Example 8.

The system and the method described above are particularly useful for heat storage, preferably for seasonal heat storage.

5 The invention makes it also possible to modify an existing system for thermochemical storage of energy, comprising a water condenser and one TCM module, by adding at least one additional TCM module. In a preferred embodiment, the additional TCM module is connected to both the water condenser and the existing TCM module. This allows the additional TCM
10 module to be used as a condenser for the existing TCM module, and to dry the additional TCM module, in turn, using the water condenser. Also other configurations are possible, as described above.

For the purpose of clarity and a concise description features are described herein as part of the same or separate embodiments, however, it
15 will be appreciated that the scope of the invention may include embodiments having combinations of all or some of the features described.

The invention will now be illustrated in the following, non-limiting examples. Parts and percentages mentioned in the examples and through the description, are by weight, unless otherwise indicated. The
20 sorption and desorption processes are illustrated using vapour pressure diagrams, which are described by the Clausius-Clapeyron equation:

$$dp/dT = \Delta h/T\Delta v,$$

wherein p is the sorbate (water) pressure, T temperature, Δh molar enthalpy and Δv molar volume differences between the phases of the
25 sorbate. In the examples, the following annotations are used: T_E evaporation temperature, p_E evaporation vapor pressure, T_S sorption temperature, B water loading (g water / g material), T_C condensation temperature, p_C condensation vapour pressure, T_D desorption temperature.

Examples

Example 1 (comparative)

5 Single stage thermochemical storage with a zeolite used as TCM

In this example, Zeolite 13X is used as TCM and water as a sorbate. The system used is depicted in Figure 1A.

10 The water vapour diagram is presented in Figure 2. In this diagram, several curves are present. The most left curve corresponds to the pure water vapour diagram, which corresponds to the conditions in the water condenser. Other curves correspond to the water vapour in a system with Zeolite Z13X with different water loadings B – particularly, from left to right, the curves are shown for $B=0.26, 0.24, 0.22, 0.20, 0.18$ g/g, *etc.*

15 The TCM module loaded with the zeolite is desorbed at $T_D = 90^\circ\text{C}$, which is a typical temperature when solar collectors are used to supply heat. The released water vapour is condensed in the water condenser at $T_C = 30^\circ\text{C}$, $p_C = 42$ mbar. This corresponds to $B = 0.22$ g water /g zeolite.

20 For the sorption reaction, water vapour is evaporated in the water condenser at $T_E = 10^\circ\text{C}$, $p_E = 12$ mbar, and the zeolite is allowed to adsorb water vapour at $T_S = 40^\circ\text{C}$, leading to $B = 0.26$ gw/gz. The difference in water loading $\Delta B = 0.04$ gw/gz, which indicates how much heat can be stored. This difference of 0.04 gw/gz corresponds to storage density $Q/M = 0.12$ GJ/ton zeolite, or $Q/V = 0.084$ GJ/m³ zeolite.

25 For further desorption of the zeolite, to lower B values, a higher T_D is necessary, which is indicated by the arrow in Figure 2.

Example 2 (comparative)

Higher thermochemical storage, one stage

5 In this example, the purpose was to obtain higher output temperatures with Zeolite 13X as TCM with thermochemical storage in one stage. The vapour pressure diagrams are shown in Figure 3A and B.

 Typically, the temperature needed for domestic hot water (DHW) is 60°C, while for space heating (SH) - 40°C.

10 As can be seen from the figures, these conditions were possible to achieve with dry Zeolite 13X (see Figure 3A, maximum sorption temperature 340 K = 67°C), but not with half-dry Zeolite 13X (see Figure 3B, maximum sorption temperature 327 K = 54°C).

 The 60°C heat should be stored separately, or in stratified boiler
15 (but not for long, as stratification disappears by heat conduction).

Example 3

Two stage thermochemical storage

20

 In this example, two identical Z13X modules M_1 , M_2 loaded with the same amount of Zeolite Z13X as the TCM are used as depicted in Figure 1B. The modules and the water condenser are connected through a central tube as explained herein-above. The water vapour diagrams are shown in
25 Figure 4.

 In a first step, both modules are dried at $T_D = 90^\circ\text{C}$ with water condenser operating at $T_C = 30^\circ\text{C}$. After that the valve between M_1 and M_2 is closed. M_1 is cooled down to 30°C, while M_2 is kept at 90°C. The heat released in M_1 can be regained by heat exchange, *e.g.* with another module
30 (<50% for concurrent and <100% for countercurrent heat exchange).

Subsequently, the valve is opened and an pressure equilibrium takes place, which leads to the drying to M_2 with M_1 . $\Delta B_2 = -\Delta B_1 = -0.045$ at $p_{eq2} = p_{eq1} = 10$ mbar. Finally, M_2 reaches water loading $B = 0.175$ gw/gz. In total $\Delta B = 0.085$ gw/gz is stored, which corresponds to storage density $Q/M =$
5 0.255 GJ/tz.

Example 4

Three stage thermochemical storage

10

In this example three identical modules M_1 , M_2 , M_3 loaded with the same amount of Zeolite Z13X as the TCM are used. The modules and the water condenser are connected through a central tube as explained herein-above. The water vapour diagrams are shown in Figure 5.

15

All the modules are first dried at $T_D 90^\circ\text{C}$ with the water condenser at $T_C = 30^\circ\text{C}$. After that, modules M_2 , M_3 are dried with M_1 to $B = 0.175$ gw/gz at $p_{eq2} = p_{eq1} = 10$ mbar, as in Example 3. In a further step, M_3 is dried with M_2 which leads to $\Delta B_3 = -\Delta B_2 = -0.065$ and equilibrium when $p_{eq3} = p_{eq2} = 2$ mbar. Finally, M_3 reaches the water loading $B = 0.11$ gw/gz. In
20 total $\Delta B = 0.15$ gw/gz is stored, which corresponds to storage density Q/M 0.45 GJ/tz.

Example 5

25

Different TCM materials: Zeolite Z13X and SG125

In this example, two TCM modules are used with different materials. One module uses Zeolite Z13X and the other one Silicagel Grace 125 of equal mass. The module with SG125 is used here as a condenser for

the zeolite module. The modules and the water condenser are connected through a central tube as explained herein-above.

The vapor pressure diagrams are shown in Figure 6, wherein the left diagram is for Zeolite Z13X and the right diagram for SG125.

5 As can be seen from Figure 6, SG125 absorbs more H₂O at lower T_C with lower increase of p_{eq}. When the Z13X module is dried with the SG125 module, $\Delta B_2 = -\Delta B_1 = 0.06$ gw/gz. In two stages 0.1 gw/gz ~ 0.30 GJ/tz.

10 Example 6

Different TCM materials: Na₂S and SG125

15 In this example, a TCM module with hygroscopic salt Na₂S is dried using a silica gel containing module. The modules and the water condenser are connected through a central tube as explained herein-above. The vapor pressure diagrams are shown in Figure 7, wherein the left diagram is for Na₂S and the right diagram for SG125.

20 A peculiarity of vapour pressure diagrams for salts able to form hydrates is that there are less curves with different water loadings, since the hydration states are limited to the number of existing hydrates. In this case, the diagram for SG125 present nearly a continuum of vapour pressure curves, while the diagram for Na₂S only shows three curves corresponding to the formation of hydrates Na₂S · 9H₂O, Na₂S · 5H₂O and Na₂S · 2H₂O. The most left curve shown is for pure water vapour.

This system allows to carry out desorption of Na₂S at 70°C instead of >90°C with *e.g.* SG125.

As an example of a suitable configuration, a single, large SG125 condenser can be used for large stock of compact Na₂S modules.

Example 7

Multiple stages of MgCl_2

5 In this example, the same thermochemical material MgCl_2 is used
in different TCM modules. The modules and the water condenser are
connected through a central tube as explained herein-above. Figure 8 shows
water vapour pressure curves for water (most left curve) and different
hydration states of MgCl_2 . (from left to right – formation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$,
10 $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ hydrates).

The method of the invention can be realized as a two stage
desorption of $\text{MgCl}_2 \cdot (6 \rightarrow 4 \rightarrow 1)\text{H}_2\text{O}$ at $T_D = 120^\circ\text{C}$ instead of 150°C . This
can also be performed as a two stage desorption of $\text{MgCl}_2 \cdot (6 \rightarrow 4 \rightarrow 2)\text{H}_2\text{O}$ at
 $T_D = 100^\circ\text{C}$ instead of 130°C . Another option is a three stage desorption
15 $\text{MgCl}_2 \cdot (6 \rightarrow 4 \rightarrow 2 \rightarrow 1)\text{H}_2\text{O}$ at 100°C .

Therefore, a lower desorption temperature can be used than when
one stage desorption is performed (see “single stage reference” in Figure 8).
This is particularly important for MgCl_2 , which is unstable at higher
temperatures.

20

Example 8

In this example a sorption method is illustrated that allows to
achieve a higher temperature T_S , which in turn can be used for higher heat
25 needs such as DHW (60°C). In this example use is made of TCM modules M_1
and M_2 and a water condenser, which works as a water evaporator. The
modules and the water condenser are connected through a central tube as
explained herein-above.

Figure 10 shows separate steps of this method. In the first step
30 (left picture) the TCM modules M_1 and M_2 are hydrated by water vapour

supplied from a cold water evaporator ($T_E = 10^\circ\text{C}$). During hydration heat is released, which brings the TCM modules at the temperature T_S 40°C . In a second step (picture in the middle), one TCM module M_1 is brought in contact with a warm water evaporator (which can be the same of different
5 as the cold water evaporator) and heats the evaporator up to T_E 40°C . In the next step (right picture), the warm water evaporator is contacted with the second TCM module M_2 to hydrate that module further, which leads to the heating of that module to $T_S = 60^\circ\text{C}$. This temperature is sufficient for typical needs for hot water (DHW).

10 Figure 11 shows the water sorption diagrams in case zeolite Z13X (Figure 11A) or SG125 (Figure 11B) is used as the thermochemical material. Figure 11A shows that for Z13X it is possible to reach $T_S' = 340$ K with water loading $B=0.26$. Figure 11B shows that for the silica gel $T_S' = 333$ K can be reached with water loading $B=0.16$.

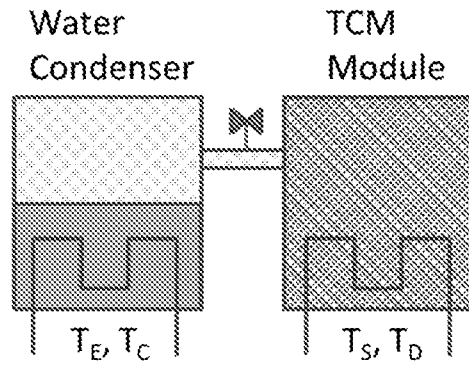
15 This example shows that with two TCM modules it is possible to reach a higher sorption temperature, which can be sufficient for DHW needs.

Claims

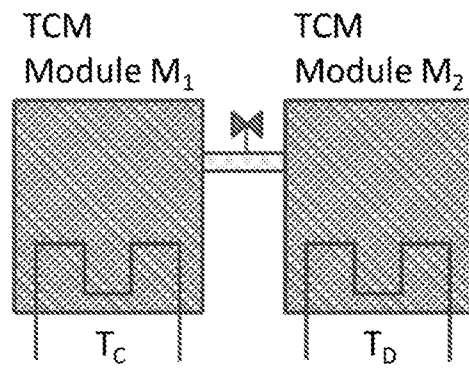
1. Closed system for thermochemical storage comprising at least one water condenser and at least two thermochemical modules, wherein a first thermochemical module comprises a first thermochemical material and a second thermochemical module comprises a second thermochemical material, and wherein the at least one water condenser and the thermochemical modules are connected so that water vapour can be exchanged individually between any two selected from the list consisting of the at least one water condenser and the at least two thermochemical modules.
2. The system according to claim 1, further comprising a connection system wherein each condenser and each TCM module has a connection through a valve with a central tube.
3. The system according to claim 1 or 2, wherein the first and the second thermochemical material are different materials.
4. The system according to any one of the preceding claims, wherein the thermochemical material is selected from the group consisting of zeolites, silica gel, hygroscopic salts, metal organic frameworks (MOF), carbon, and aluminum phosphates.
5. The system according to claim 4, wherein the hygroscopic salt is selected from the list consisting of chlorides, sulfates, iodides, nitrates, sulfides and its hydrates.

6. The system according to any one of the preceding claims, comprising further a third thermochemical module comprising a third thermochemical material.
- 5 7. Method for desorption in a system for thermochemical storage according to any one of claims 1-6, comprising a step wherein the desorption in the second thermochemical module is realized using at least the first thermochemical module as a condenser.
- 10 8. The method according to claim 7, comprising a further step, wherein the desorption in the first thermochemical module is realized using the water condenser.
9. The method according to claim 7 or 8, wherein the system
15 comprises a third thermochemical module and the desorption in the third thermochemical module is realized using either of the first thermochemical module or the second thermochemical module as a condenser or using the water condenser.
- 20 10. The method according to claim 7 or 8, wherein the system comprises a third thermochemical module and the desorption in the third thermochemical module is realized using both the second and the first thermochemical modules as a condenser.
- 25 11. The method according to any one of claims 7-10, wherein the thermochemical material is selected from the group consisting of zeolites, silica gel, hygroscopic salts, metal organic frameworks (MOF), carbon, and aluminum phosphates.

12. Method for sorption in a system for thermochemical storage according to any one of claims 1-6, comprising a step wherein the sorption in the second thermochemical module is realized using at least the first thermochemical module as an evaporator.



(A)



(B)

Figure 1

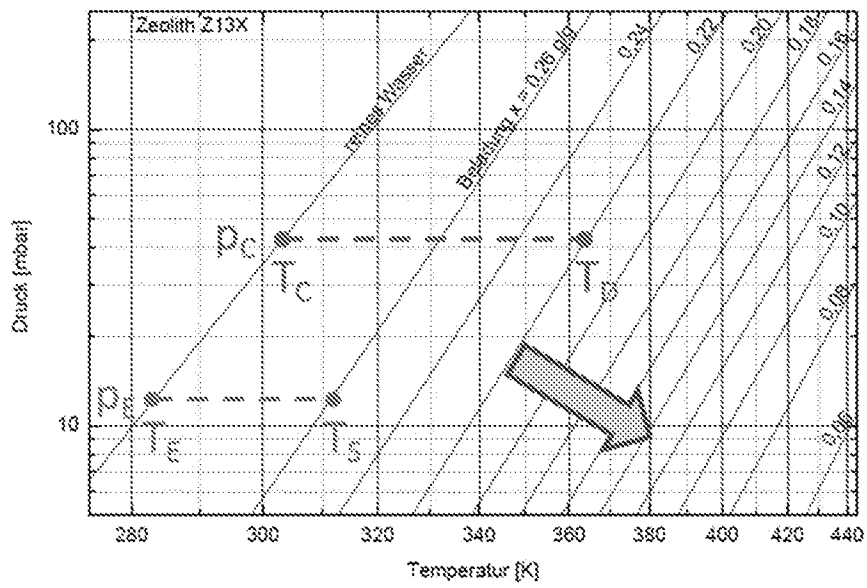
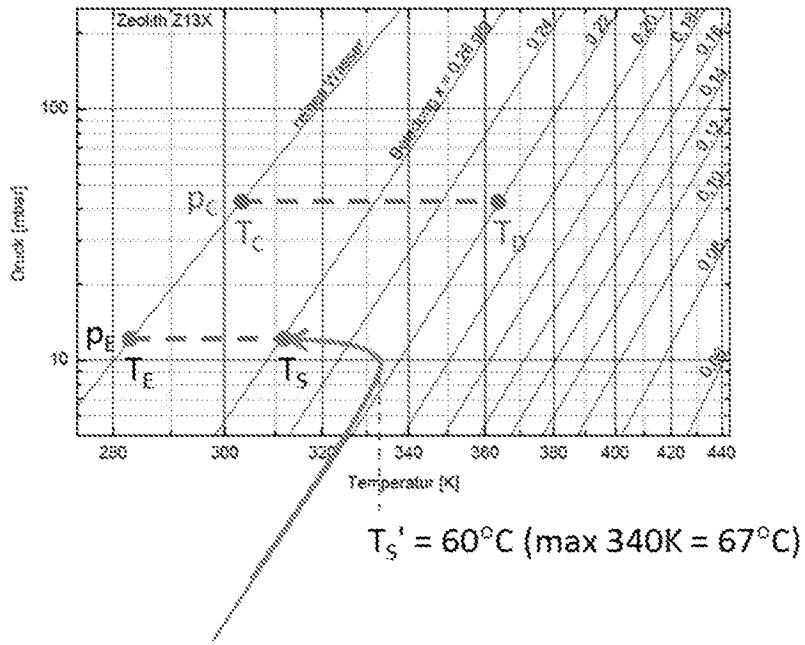


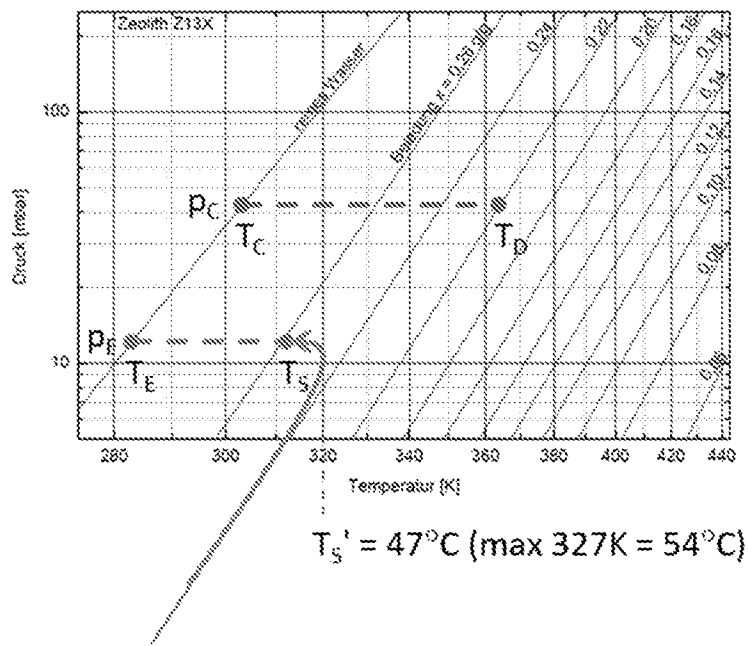
Figure 2

With dry Z13X, B = 0.22



(A)

With half-dry Z13X, B = 0.24



(B)

Figure 3

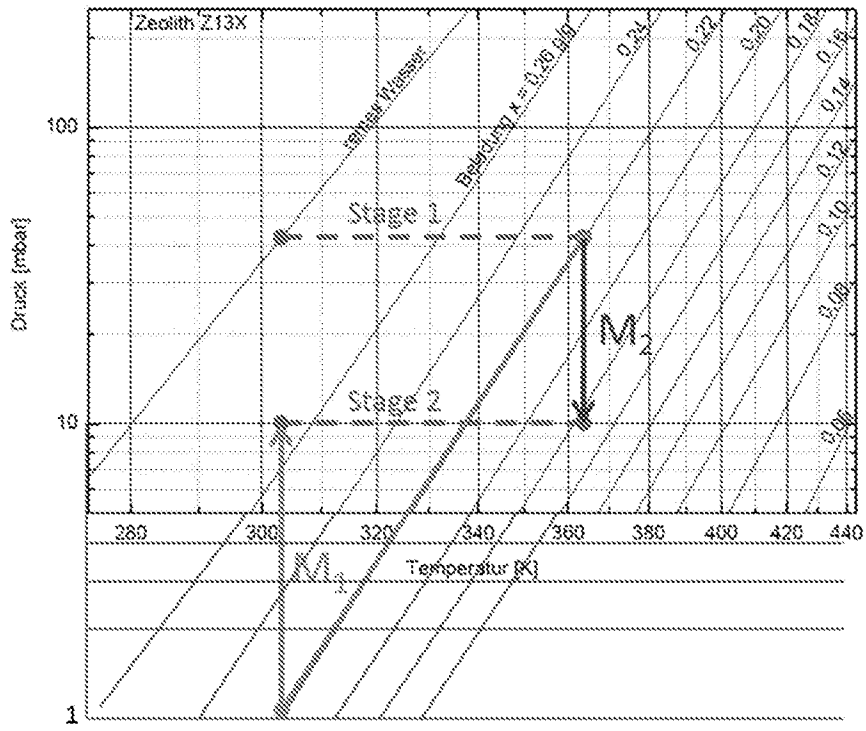


Figure 4

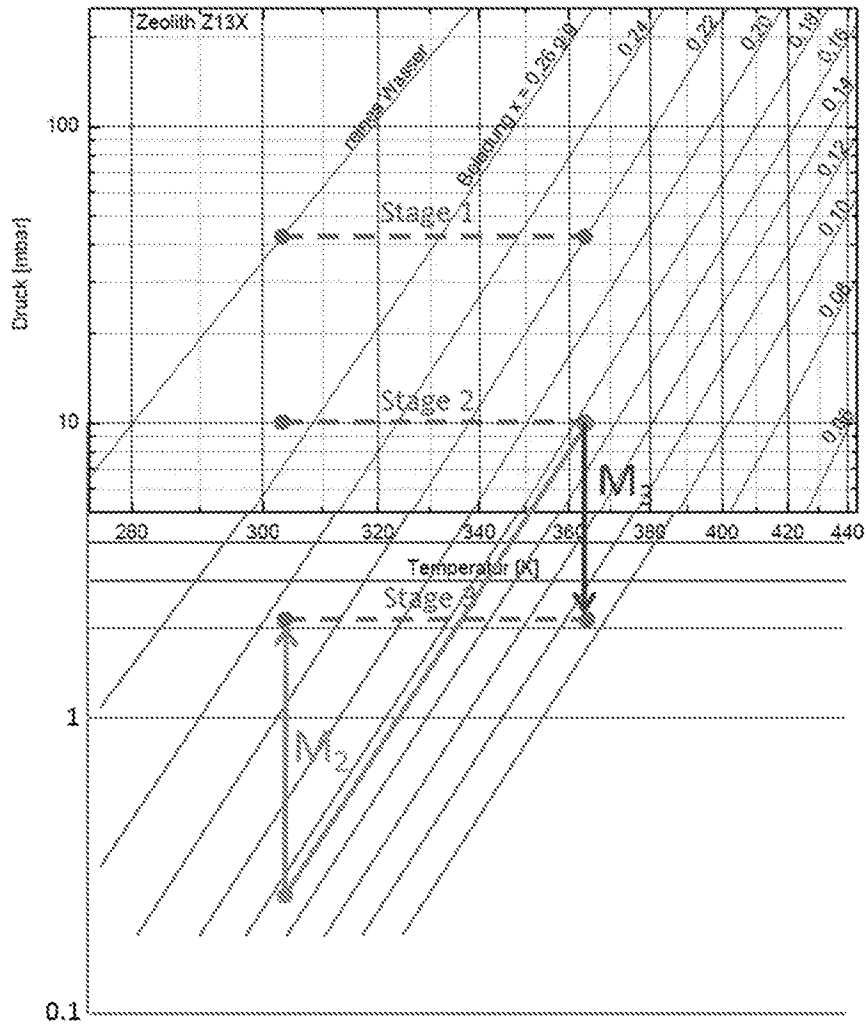


Figure 5

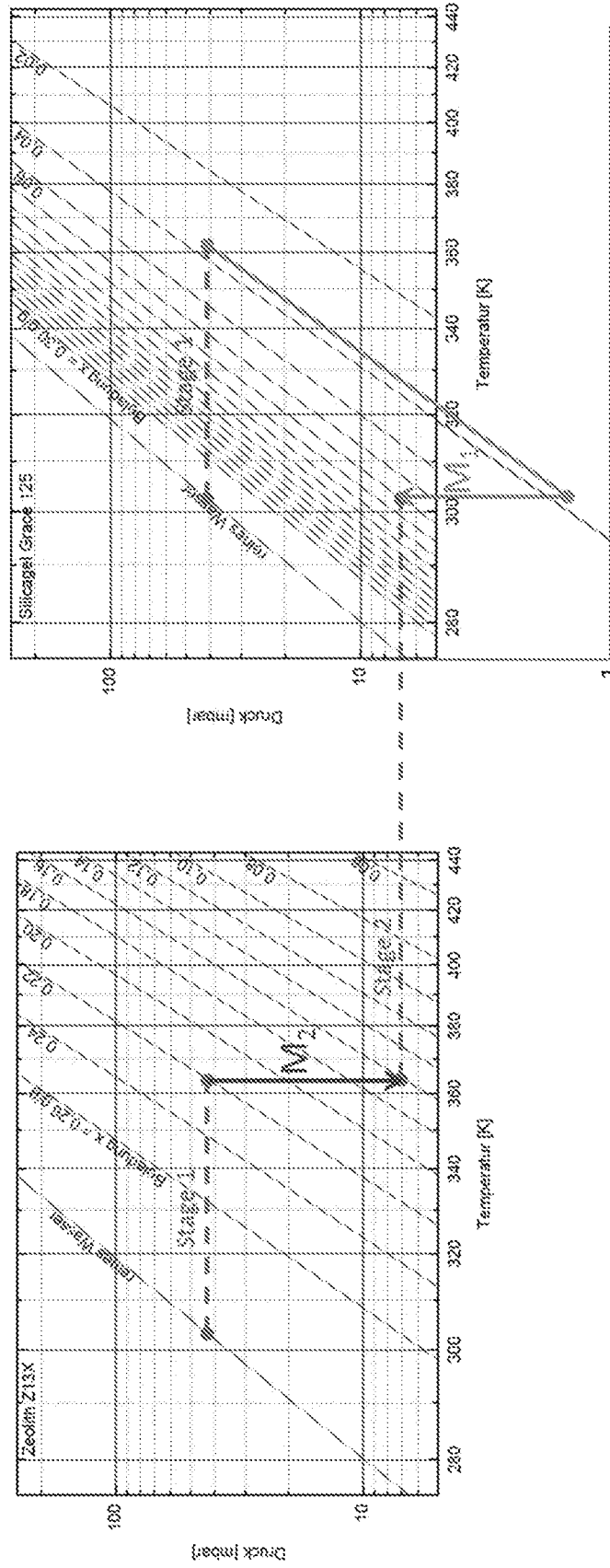


Figure 6

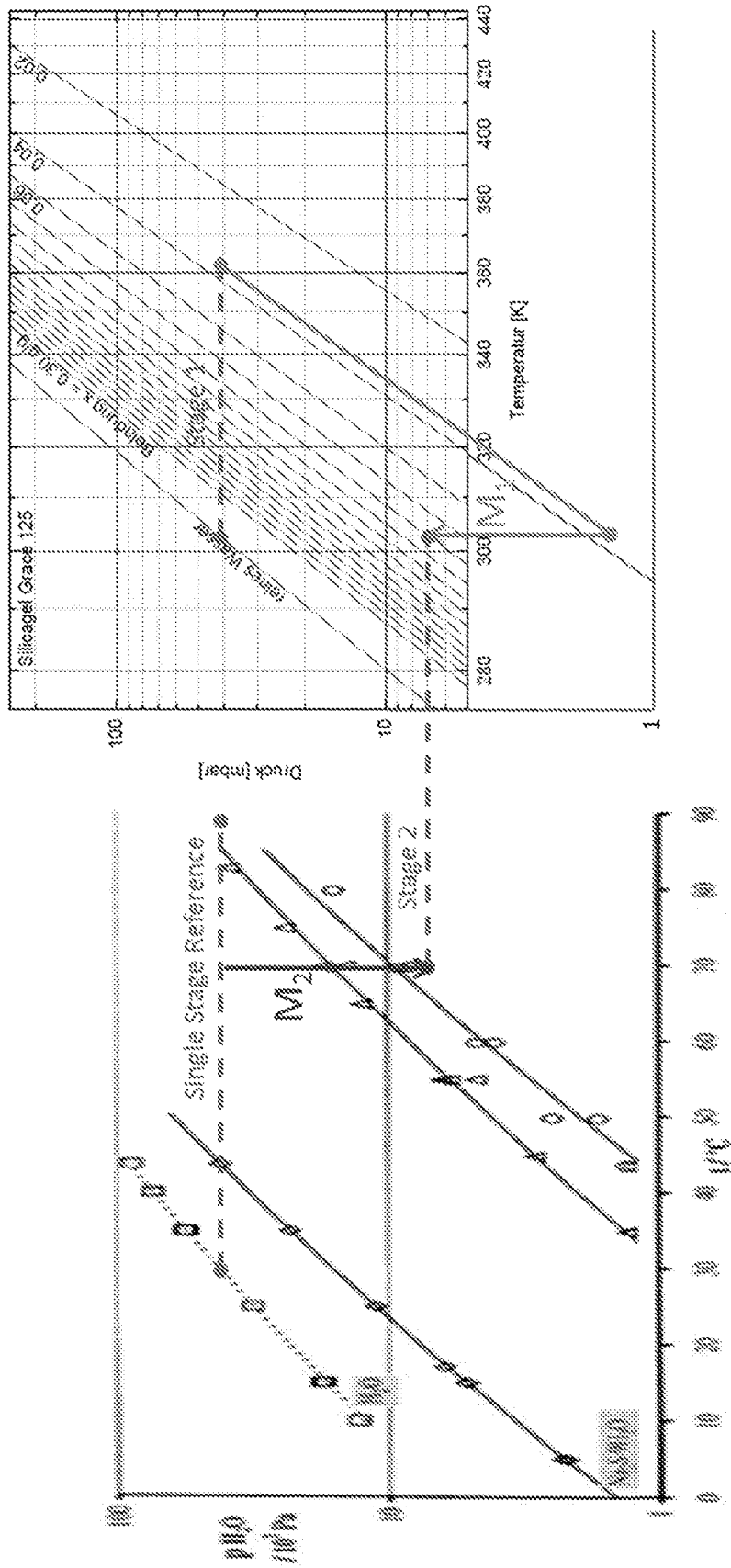


Figure 7

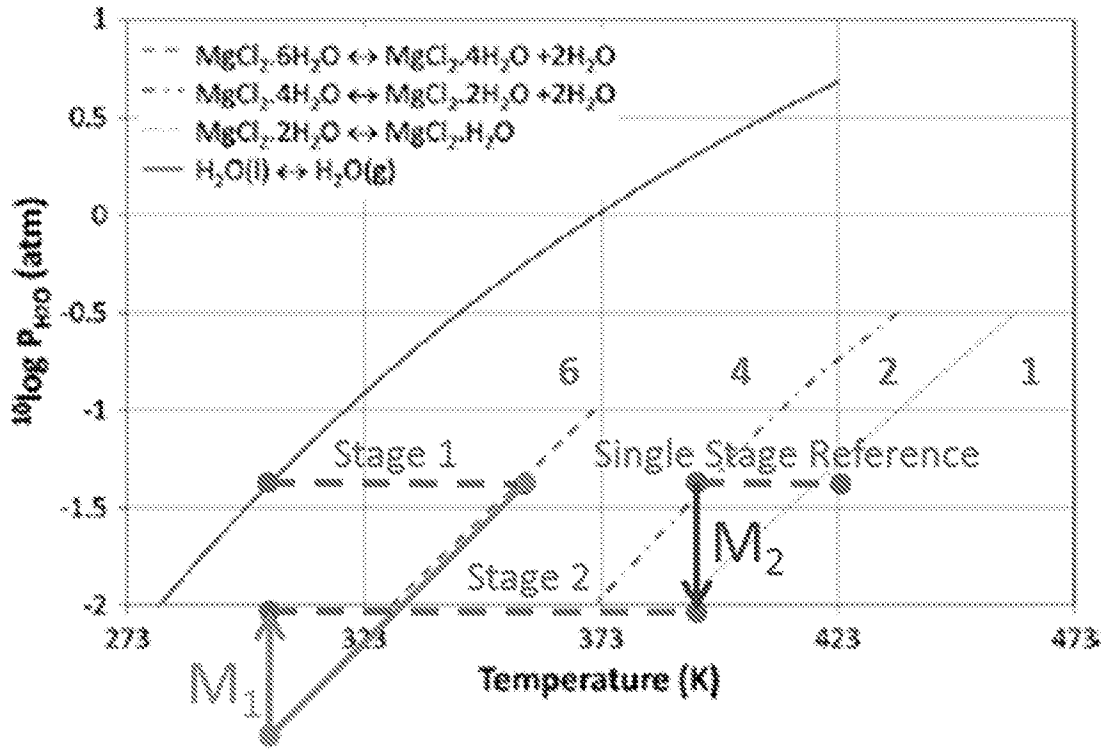


Figure 8

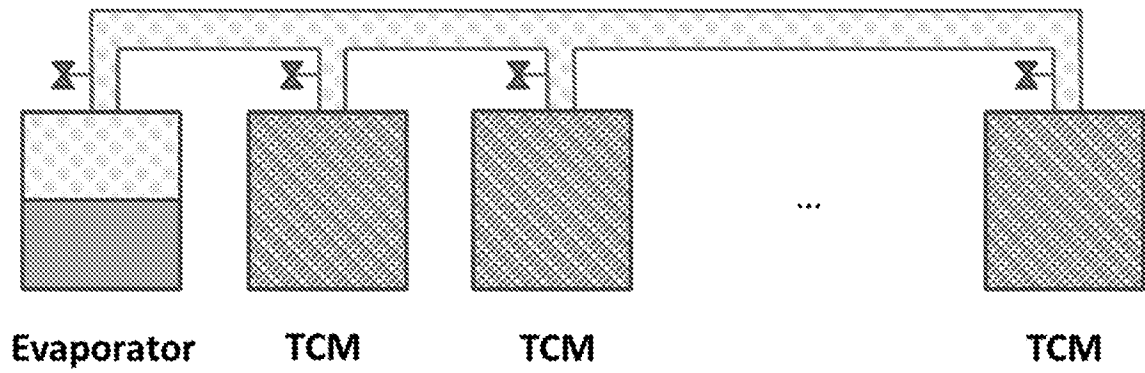


Figure 9

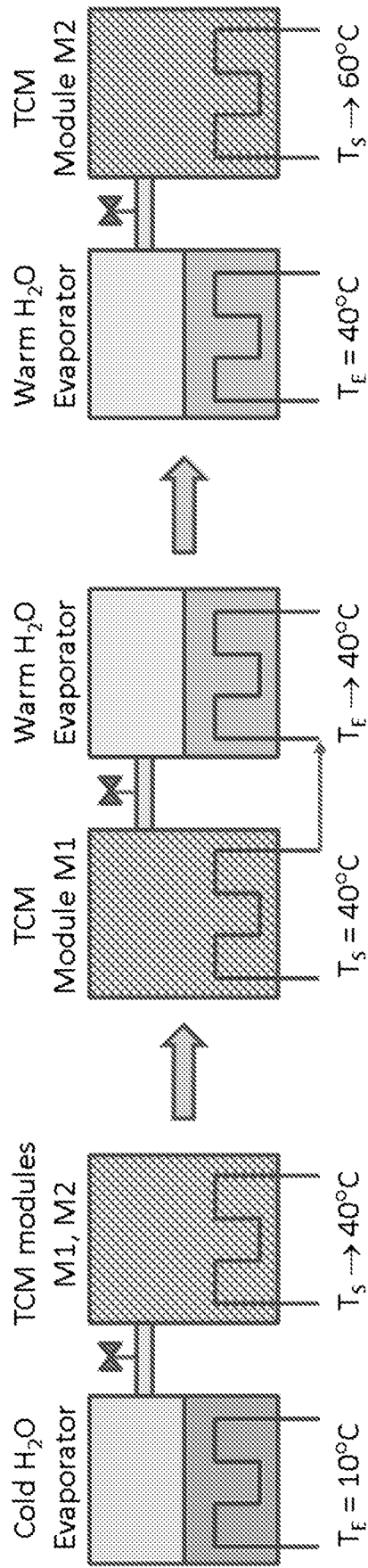
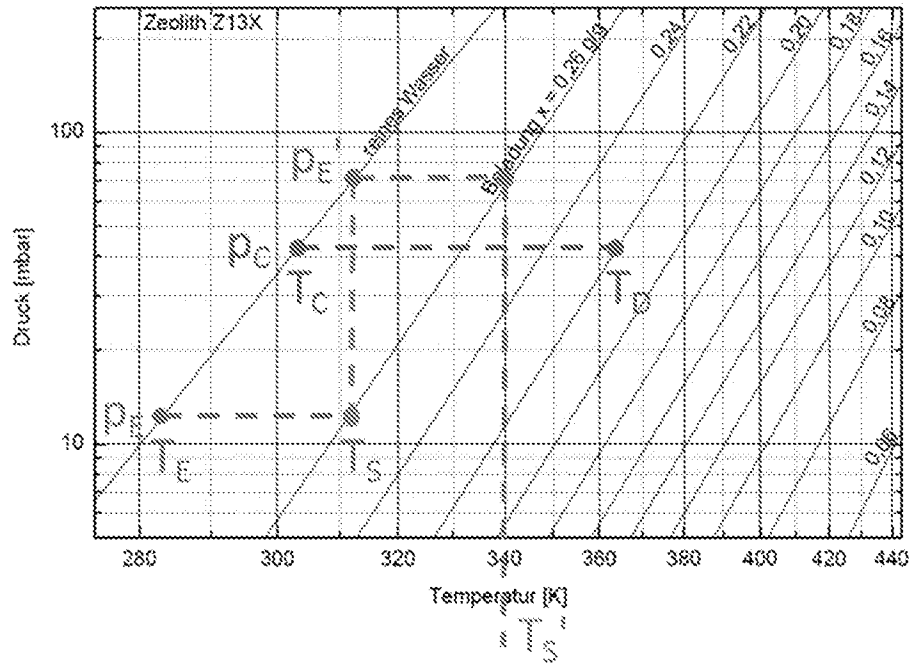
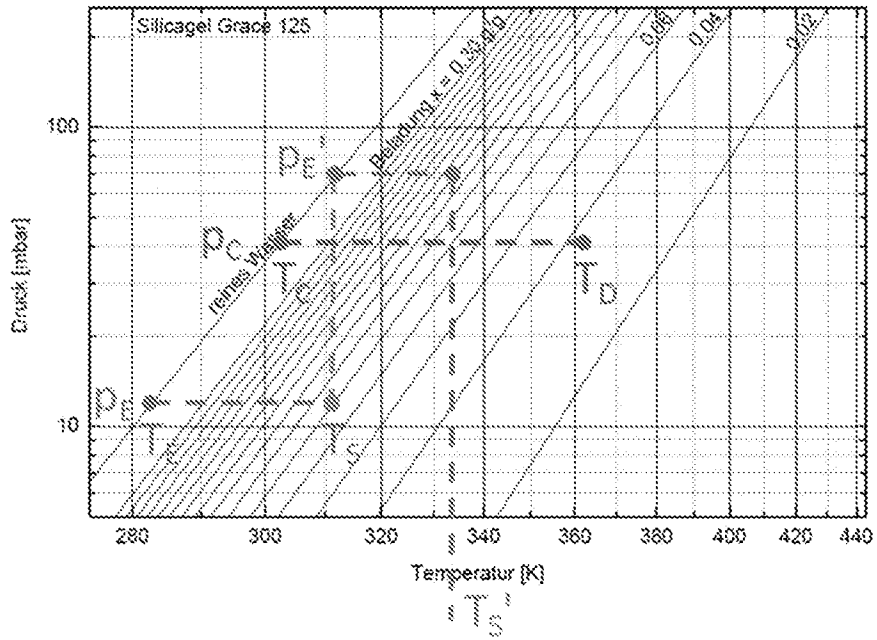


Figure 10



(A)



(B)

Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2015/050604

A. CLASSIFICATION OF SUBJECT MATTER
 INV. F28D20/00 F25B17/08
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 F28D F25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/251394 A1 (KOMAKI KATSUYA [JP] ET AL) 4 October 2012 (2012-10-04) abstract; figures 1,5,7 paragraphs [0031], [0041] -----	1
X	US 6 041 617 A (SANADA MASARU [JP] ET AL) 28 March 2000 (2000-03-28) column 1, line 34 - line 51; figures 8,11 -----	1,4
X	EP 2 674 696 A1 (TOYOTA CHUO KENKYUSHO KK [JP]) 18 December 2013 (2013-12-18) abstract; figure 7 paragraphs [0005], [0016] paragraph [0078] - paragraph [0083] -----	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 3 February 2016	Date of mailing of the international search report 10/02/2016
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Martínez Rico, Celia
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2015/050604

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			WO 2012108288 A1	16-08-2012
