Systematic search algorithm for potential thermochemical energy storage systems

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HIGHLIGHTS

• An automated search for reaction systems suitable for thermochemical energy storage was performed.
• Algorithm to build reaction systems for thermochemical energy storage is presented.
• Close to 1000 possible reaction systems for 5 different reactive gases were found.
• The VIENNA TCES-database for thermochemical energy storage materials is presented.

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ABSTRACT

Thermochemical energy storage (TCES) is considered as an emerging green technology for increased energy utilization efficiency, thereby achieving a reduction of greenhouse gases. Various reaction systems based on different substance classes (e.g. hydrates, hydroxides, oxides) were suggested and investigated so far. Nevertheless, the number of known reactions which are suitable is still limited, as the main focus concentrates on the investigation of a handful known substances, their further improvement or applicability. To find novel promising candidates for thermochemical energy storage and also to allow for a broader view on the topic, this work presents a systematic search approach for thermochemical storage reactions based on chemical databases. A mathematical search algorithm identifies potential reactions categorized by the reactant necessary for the reaction cycle and ranked by storage density. These candidates are listed in the online available VIENNA TCES-database, combined with experimental results, assessing the suitability of these reactions regarding e.g. decomposition/recombination temperature, reversibility, cycle stability, etc.

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1. Introduction

Research on the topic of thermochemical energy storage (TCES) has experienced an increased perception in the last few years. This is primarily driven by the possibility to reduce CO₂ emission by energy savings in buildings and industrial sectors and reducing waste thermal energy on a national and continental scale [1]. In this context TCES is of special interest due to its applicability in a wide temperature range and for a variety of applications.

The International Energy Agency (IEA) distinguishes three temperature levels for heat: low (<100 °C), medium (100–400 °C) and high (>400 °C) [2].

The low temperature level represents the typical household application. There, TCES can be used for heating and cooling, often in combination with solar energy [3].

The medium temperature level comprises mainly waste heat sources from industrial applications, which are a major cause of energy inefficiency [4]. Waste heat occurs when heat is used within production processes either in form of process steam or in fired furnaces [5]. In electricity production about 66% of the total primary energy input are lost during the conversion from heat to electricity [6]. A higher conversion rate to electricity is hampered by the comparably low efficiency of the available processes (e.g.
the energy efficiency of the organic rankine cycle (ORC) process at the cement plant in Lengfurt, Germany, is at only 12.8% [7]. The use of waste heat as heat itself is often not possible due to the fact that supply and demand cannot be matched temporally or the distances between producer and customer are too large [8]. TCES can be used to improve the energy efficiency of processes, by bridging the temporal and/or spatial gap between the producer of waste heat and potential consumer (e.g. from the heat production site to a local heating district or in a batch process, from the cool down of one cycle to the heat up of the next) [9].

In the high temperature level TCES can be used for specialized applications. In cars 60% of the fuel energy are lost as heat, mostly through the exhaust at a temperature up to 800 °C [10]. TCES can be used to recuperate parts of this energy and use it for minimizing the warm-up period of the exhaust track at the next cold start [11]. TCES can also be combined with concentrating solar plants to increase their production into times with low sunlight (e.g. when the sun is blocked by clouds or after sunset) [12,13]. For this application materials for temperatures of 800 °C or higher are needed.

TCES is based on a reversible chemical reaction (1). Heat is consumed, while decomposing material A into two products B and C, thus storing the reaction energy \( \Delta H_R \) in the products. To discharge the system, both products B and C react under formation of A, now releasing the stored energy.

\[
v_A A(s) + \Delta H_R = v_B B(s) + v_C C(g)
\]

(1)

The direction of the reaction, which strongly depends on temperature, is given by the sign of the Gibbs energy \( \Delta G_R \):

\[
\Delta G_R^T = \Delta H_R^T - T \Delta S_R^T
\]

(2)

with \( \Delta H_R^T = \sum v_i \Delta H_i^T \) and \( \Delta S_R^T = \sum v_i \Delta S_i^T \), where \( \Delta S_i \) being the reaction entropy (it can be assumed that \( \Delta S_R > 0 \) for the given notation of reaction (1)). If the reaction is in equilibrium then \( T = T_{equ} \) and \( \Delta G_R = 0 \). For \( T > T_{equ} \) follows that \( \Delta G_R < 0 \), which means the system reacts from left to right (decomposition), if \( T < T_{equ} \) then \( \Delta G_R > 0 \) and the system reacts form right to left (recombination). The equilibrium temperature \( T_{equ} \) can be calculated iteratively from (2) by

\[
T_{equ} = \frac{\Delta H_{R_{equ}}}{\Delta S_{R_{equ}}} = \frac{\sum v_i \Delta H_i^{R_{equ}}}{\sum v_i \Delta S_i^{R_{equ}}}
\]

(3)

Since \( \Delta H_i^T \) and \( \Delta S_i^T \) differ for each substance, each reaction system has a specific \( T_{equ} \). For an efficient use of TCES it is crucial that the equilibrium temperature of the applied reaction system fits to the temperature level of the heat source.

The fundamental process for TCES is depicted in Fig. 1. The charging reaction occurs in reactor 1, thereby decomposing the storage material A to B following reaction (1). Depending on the reaction system it may be necessary to store the produced gas C. The heat input is generally realized using a carrier gas. It is obligatory that the carrier gas is inert in terms of the reaction system, so no side reactions occur. The charged material B reacts with C back to A in reactor 2, releasing the previously stored energy. Again, in most processes a heat carrier gas will be used to transport the heat out of the reactor 2, which can be the reactive gas itself or an inert gas. It has to be noted that the temperature in reactor 1 \( T_1 \) has to be above \( T_{equ} \) of the reaction kinetic of the reaction system, while in reactor 2 it has to be vice versa (\( T_2 < T_{equ} \)) at the given process conditions. The required temperature spread \( T_2 - T_1 \) strongly depends on the reaction system and the process conditions. Reactors 1 and 2 can be located at different sites with a material transport system between them, e.g. trucks transporting the material. Another possibility would be to use only one reactor for both charging and discharging at different times in a batch process. Thus, on-site material storage would be needed for this case.

There are various reaction systems in development at the moment. For the low and middle temperature level mainly salt hydrates [14], like CaCl₂·6H₂O/CaCl₂ [15,16] and MgSO₄·7H₂O/MgSO₄ [17,18] are currently investigated. Pardo et al. [19] concluded that the most promising reaction systems for the high temperature level are Ca(OH)₂/CaO [20] and PbCO₃/PbO [21]. For solar applications, also reactions of metal oxides are shifting in the focus of the research [22,23].

The wide temperature range in which TCES can be utilized and the diversity of the reactions applicable for TCES create the necessity of a comprehensive database with different TCES reaction systems. This database helps the consumer to select an appropriate TCES reaction system for a given application purpose. The basis for such a database is a systematic screening to find reaction systems for a wide temperature range. So far, only one systematic approach to screen for TCES materials is known to the authors. NTsoukpoe et al. performed a systematic evaluation of 125 salt hydrates for TCES at low temperature levels with the main focus on a household application. They first discriminated based on material safety and past experiences, then focused on thermal analysis to find suitable candidates for TCES. The 125 salt hydrates where identified using a thermochromochemical database, but no detailed information on how they were identified was given [24]. In this work, reaction systems were identified for a broad temperature range (25–1000 °C). The use of an algorithm to find reaction systems results in an objective, comprehensive list, which is not based on prior knowledge of the researcher.

2. Search for potential storage systems

2.1. Goal of the search

With this systematic search approach for potential TCES systems the goal of the authors is the provision of an TCES database, where different kinds of principally suitable TCES reactions, sorted by temperature regime regarding their potential applicability, are listed. The entries in the database include products and educts of the reaction, equilibrium temperatures and, for selected promising candidates, also experimental data regarding material properties, reversibility of the TCES reaction, cycle stability and storage density. In a second step thermodynamic data and kinetic information will be supplemented. Below, the database search algorithm yielding potential TCES systems is described, for further details on the database see Section 3.

2.2. Basis of the search

The focus of this work lies on the search for potential TCES systems. In this first approach the search was narrowed to reactions of solid inorganic substances with a reactive gas, following general reaction

\[
v_A A(g) + v_B B(s) + v_C C(g)
\]

(4)
The focus on solid/gas reaction was done due to the fact that it is easy to separate the gaseous component from the solid one, ensuring energy storage over a long period by preventing reverse reaction. In contrast, for solid/liquid systems the separation is more energy consuming, resulting in a reduced storage capacity. Additionally, solid/liquid systems are contend with solubility of the solid reactants [25]. Furthermore only one gaseous component is allowed avoiding the need of a gas separation. The focus on inorganic substances was necessary due to the limitations of the search algorithm. While inorganic reactions can be identified by comparison of molecular formulas, for most organic reactions the structural formula of each reactant has to be considered. This would result in a steep increase in the complexity of the search algorithm and was therefore neglected in this approach.

2.2.1. Materials
In this first approach, building the basis of our database, a sum of 4528 different materials was taken into account as possible thermochemical energy storage materials. The thermodynamic data was gathered from HSC Chemistry database [26].

2.2.2. Reactive gases
As outlined before our selection was limited to gas-solid reactions. The reactive gases in this work were limited to H_2O, CO_2, O_2, NH_3 and SO_2, as those are all commercially used reactive gases used on industrial scales. Additionally, risks and safety issues regarding handling and storage are known. Due to intrinsic problems on storage and handling H_2 was excluded as a reactive gas.

2.3. Search algorithm
To find reaction systems suitable for TCES, an algorithm was designed to find all possible reactions for a given set of materials. The algorithm identifies all possible decomposition reactions within the selected boundary conditions (maximal allowed stoichiometric coefficient) represented by reaction (4).

$$\text{Fig. 2 shows a graphical visualization of the algorithm. It consists of 3 loops to determine the stoichiometric indices } \nu_A, \nu_B, \text{and } \nu_C \text{ based on examples. The concept behind the search algorithm is the rearrangement of a stoichiometric equation. From a mathematical point of view reaction (4) is identical to reaction (5).}$$

$$\nu_A A(s) - \nu_C C(g) = \nu_B B(s)$$

Hence, a stoichiometric correct reaction is obtained, if the subtraction of reactive gas C from substance A results in an elemental composition EC, for which a substance B can be found in the database.

In case of reaction (6), the subtraction of the elemental composition of H_2O (2H, 1O with 1 and 2 being the elemental indices) from the elemental composition of Mg(OH)_2 (1Mg, 2O, 2H) results in a composition (1Mg, 1O) which correlates to the database entry of magnesia oxide MgO.

$$\text{Mg(OH}_2 = \text{MgO + H}_2\text{O}$$

To identify reactions which require multiple subtractions of C, (see reaction (7)) the stoichiometric coefficient \(\nu_C\) is increased incrementally until the subtraction is no longer possible (loop II). During each iteration, the resulting EC is checked against the database. A positive hit in the database is followed by the output of the corresponding substances as suitable TCES reaction. Subsequently or on a negative database request, the loop is repeated until the calculation of EC is no longer possible.

Ca(NH_3)_2Cl_2 \rightarrow CaCl_2 + 8NH_3 \hfill (7)

If a subtraction of \(\nu_C\)-times of C is not possible for the current \(\nu_C\), the algorithm increases the stoichiometric coefficient \(\nu_C\) incrementally and starts again to subtract one C (loop I). This is necessary to find reactions like reaction (8), where more than 1 molecule of A is needed to obtain a balanced reaction equation with integers. Loop I is repeated until \(\nu_A > \nu_{A,\text{max}} (\nu_{A,\text{max}}\text{ is given by the user).}$$

$$2\text{NaOH} = \text{Na}_2\text{O} + \text{H}_2\text{O}$$

To identify reactions with \(\nu_A \neq 1\), like reaction (9), the calculated EC of each subtraction is further analyzed in loop III (Fig. 3).

$$6\text{Mn}_2\text{O}_3 = 4\text{Mn}_3\text{O}_4 + \text{O}_2$$

Therefore, the highest possible value for \(\nu_A, \nu_{A,\text{max}}\), is determined based on the calculated elemental composition EC. In case of reaction (9) \(EC = 12\text{Mn}\) and 160 based on (5) with \(\nu_A = 6\) and \(\nu_C = 1\). \(\nu_{A,\text{max}}\text{ is calculated as the lowest elemental index of } EC, \text{since it is the highest integer still able to divide } EC \text{ without remainder. In this case } \nu_{A,\text{max}} = 12 \text{ due to Mn.}$$

To find all possible combinations, at first, a reaction with \(\nu_A = 1\) is assumed. An intermediary elemental composition is calculated as \(EC' = EC/\nu_A\). \(EC'\) is checked against the database to find a substance with a matching elemental composition. Then \(\nu_A\) is increased by one. If the division of all elemental indices of EC with the new \(\nu_A\) is possible without a remainder (ECmodnu = 0), another possible elemental composition \(EC'' = EC/\nu_A\) is found and subsequently checked against the database. This is repeated until \(\nu_A > \nu_{A,\text{max}}\). For reaction (9) all possible \(\nu_A\) and the corresponding elemental compositions \(EC''\) are given in Table 1. Only for \(\nu_A = 4\) can a substance with a matching elemental composition (Mn_3O_4) be found in the database.

It should be noted, that this approach identifies all numerically possible reactions. The further discrimination of these hits regarding their chemical significance is given in Section 3.5.

3. Results
The search for each reactive gas was performed with \(\nu_{A,\text{max}} = 6\) to cover reactions like reaction (9). For the five reactive gases (H_2O, CO_2, NH_3, SO_2, O_2) more than 1700 unique reactions were found. A comprehensive list of all reactions can be found on the project homepage.\(^1\) For each reaction the equilibrium temperature \(T_{\text{equ}}\) has been calculated following (3) based on the thermodynamic data from HSC database.

For a reaction principally suitable as TCES system two criteria have to be met:

$$\Delta G_{R}^{25\text{C}} > 0 \hfill (10a)$$
$$\Delta H_{R}^{\text{rev}} > 0 \hfill (10b)$$

Criterion 1 (10a) defines the decomposition reaction for 25 °C as disfavoured, thus non-spontaneous. Therefore, at room temperature no decomposition will occur, which is obligatory for storage without energy loss. Criterion 2 (10b) follows the requirement that the reaction is endothermic at \(T_{\text{equ}}\) and therefore capable of storing energy while it decomposes. Additionally, at this point only reactions with \(T_{\text{equ}}\) within the range of 25–2000 °C are considered relevant.

Thereby, the number of potential TCES systems is reduced to 1185 reactions. Table 2 gives the number of identified reactions per temperature level for each reactive gas based on \(T_{\text{equ}}\). In Fig. 4 the distribution of the identified reactions is shown. The energy content is calculated as \(\Delta H_{R}\) at \(T_{\text{equ}}\) for one kilogram of sub-

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\(^1\) solidheat.project.tuwien.ac.at.
stance A of each reaction, therefore representing the theoretical energy amount stored in 1 kg material in its discharged state. Due to the high number of identified reactions with H$_2$O, those reactions are separated into reactions of hydroxides and metal hydrates.

A comparison of the different reactive gases is given in Fig. 5. The area for each gas marks the range where the majority of reactions are identified. To take into account that reactions with a higher $T_{eq}$ are more sparse than with lower $T_{eq}$, as seen in Fig. 4, the reactions identified for each reactive gas were clustered. Fig. 6 shows the clustering exemplary for the reactions of hydroxides. First two clusters were calculated, utilizing k-means clustering based on the normed euclidean distances [27]. Then, from each cluster 80% of the reactions closest to the corresponding cluster centre are together surrounded by one convex hull. The line in Fig. 6 is equivalent to the line for H$_2$O-hydroxides in Fig. 5. In the following the identified reactions for different reactive gases are discussed further.
the oxidation of FeS with O$_2$ occurs according to reaction (11b), metrically correct, but chemically they will not occur. For example, of the search algorithm reactions are identified which are stoichiometrically correct but chemically nonsense, they were separated as they are more unlikely to occur. Reactions (12) illustrate this, as reaction (12b) is kept. This leads to additional 104 reactions with O$_2$ for further investigation (173 reactions were removed).

The search with H$_2$O as reactive gas resulted in 553 identified reactions. They consist of reactions of metal hydroxides (47 reactions) and metal salt hydrates (506 reactions). The metal salt hydrates can be reduced to 206 decomposition reactions of different materials, excluding changes between different hydrate contents. As shown in Fig. 5, the reactions of metal salt hydrates mostly occur in a temperature range from room temperature to 500 °C, while the decomposition reactions of metal hydroxides can be found up to 1000 °C.

3.1. Reactions with H$_2$O

The search with H$_2$O as reactive gas resulted in 553 identified reactions. They consist of reactions of metal hydroxides (47 reactions) and metal salt hydrates (506 reactions). The metal salt hydrates can be reduced to 206 decomposition reactions of different materials, excluding changes between different hydrate contents. As shown in Fig. 5, the reactions of metal salt hydrates mostly occur in a temperature range from room temperature to 500 °C, while the decomposition reactions of metal hydroxides can be found up to 1000 °C.

3.2. Reactions with CO$_2$

In total 40 reactions of CO$_2$ as reactive gas were identified. This class consists mainly of carbonates and a few oxalates, having equilibrium temperatures distributed over the whole temperature range.

3.3. Reactions with NH$_3$

NH$_3$ as reactive gas yielded 39 decomposition reactions of 12 different metal salts, all of them having various coordination numbers of ammonia. The equilibrium temperatures are found between room temperature and 600 °C.

3.4. Reactions with SO$_2$

The search for reactions with SO$_2$ found 28 possible reactions, all reactions of metal oxides forming sulfates or sulfites. They are found in a temperature range between 400 and 1500 °C.

3.5. Reactions with O$_2$

Looking at reaction (11a) it is evident that due to the approach of the search algorithm reactions are identified which are stoichiometrically correct, but chemically they will not occur. For example, the oxidation of FeS with O$_2$ occurs according to reaction (11b), rather than (11a). But as reaction (11b) cannot be generalized via the approach of reaction (5), it is therefore not identified by the algorithm.

FeS + 2O$_2$ = FeSO$_4$ (11a)
4FeS + 11O$_2$ = 2Fe$_2$O$_3$ + 8SO$_2$ (11b)

In order to reduce the number of reactions, which are stoichiometrically correct but chemically nonsense, they were separated into two classes. The first class included reactions where only O$_2$ and a metal are involved. This resulted in 248 reactions, which can be further divided into reactions involving an elemental metal (65 reactions) and reactions, where the solid components are both metal oxides, undergoing a change in the oxidation stage of metal (oxides) or the oxygen (peroxides) (overall 183 reactions). All these reactions are assumed to be chemically meaningful.

The second class includes reactions where oxygen, a metal and a non-metal element are involved (like (12)). It can be assumed that reactions where the oxidation number of the non-metal element changes from positive to negative can be eliminated for a first approach as they are more unlikely to occur. Reactions (12) illustrate this, as reaction (12b) is kept. This leads to additional 104 reactions with O$_2$ for further investigation (173 reactions were removed).

2KClO$_4$ = 2KClO$_3$ + O$_2$ (12a)
KClO$_4$ = KCl + 2O$_2$ (12b)

4. Discussion

Using the HSC database as source for the systematic search algorithm, a notable list of reactions principally suitable as TCES materials was identified (see Section 3). This list is by no means complete, but reflects the general behaviour of the reactions with the different reactive gas. From Fig. 5 one can see that reactions systems of both H$_2$O-hydrates and NH$_3$ are limited to lower temperature levels. This results from the coordinative bond of H$_2$O and NH$_3$, respectively, which has a generally lower binding energy compared to covalent bonds of the reaction gases in other reaction systems. The lower binding energy induces a lower thermal stability, causing materials with coordinative bound H$_2$O or NH$_3$ to decompose earlier. On the other hand, materials that form covalent bonds are capable of forming multiple bonds per unit cell, e.g. MgSO$_4\cdot$7H$_2$O can form 7 bonds per unit cell, thus storing the binding energy of a coordinative bond multiple times. The combination of both properties leads to high energy contents with low equilibrium temperatures, making both groups of reactions ideal for low temperature applications. Reactions of metal hydroxides seem to be disadvantageous compared to hydrate or amine reactions, due to their lower energy content, but since often not all coordinative bonds of hydrate or amines can be utilized for energy storage, metal hydroxides also pose possible options for TCES systems. For high temperature application, reactions with O$_2$, CO$_2$ and SO$_2$ are generally applicable, with the reactions with O$_2$ having an advantage in the realization as a result of the availability of O$_2$. To further discriminate the reactions for their suitability as a TCES system experimental investigation is necessary.

For selecting materials which would be suitable for a first experimental investigation the identified reactions were filtered according to following criteria:

1. reactions with a theoretical T$_{eqp}$ < 1000 °C
2. reactions with an energy density higher than 2 GJ/m$^3$
3. reactions allowing for proper handling (thus avoiding liquid or molten decomposition products, unstable or highly corrosive reactants/products)

The first criterion was applied, since it is unlikely that heat with a temperature level above 1000 °C is available for storage. The sec-
ond criterion removes all systems with a low heat storage capacity since the heat storage capacity directly correlates with the economic feasibility of the system. Criterion 3 ensures that the found systems follow the general reaction (4). To a minor extent also availability, toxicity and finally the price were considered. Other properties like reversibility and cycle stability, which both are mandatory for a working TCES material, have to be checked individually for each systems, since they cannot be calculated from thermodynamic data. Moreover, important characteristics of the system like the interaction with the containing material and sintering behaviour can only be assessed in context of a specific application. To further assess their real potential as TCES material, different analytical techniques were applied. Temperature dependent powder X-ray diffraction (P-XRD) under different (reactive

![Fig. 4. Hit distribution maps for the different reactive gases. The colour corresponds to the number of reactions identified in the cell. Each cell has a width of 100 °C and a height of 0.33 MJ/kg. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
The reactions entered in the VIENNA TCES-database are selected from chemistry databases; so far the HSC database was used as source. By the use of a systematic search algorithm potentially suitable candidates for TCES reactions were identified. The algorithm screens for reaction couples, where both educts and products have a database entry and can be matched via mathematical analysis of the corresponding elemental coefficients. Nevertheless, a control eliminating stoichiometric correct couples, where a reaction cannot occur, has to avoid chemically nonsense entries. According to this approach, and limited to gas-solid reactions, for a combination of five reactive gases led to 1012 principally suitable TCES materials (H₂O 553 hits, CO₂ 40 hits, NH₃ 39 hits, SO₂ 28 hits and O₂ 352 hits).

Those materials were filtered based on their equilibria temperature, energy density, reversibility and manageability. To further assess their potential as TCES material P-XRD and STA measurements were performed, which will be published subsequently as full papers.

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