Thermochemical Energy Storage Concept Based on a Reactor Cascade with Different Storage Materials

Stylianos Flegkas¹*, Felix Birkelbach¹, Andreas Werner¹, Norbert Freiberger², Markus Haider¹, Franz Winter³, Peter Weinberger⁴

¹) Institute for Energy Systems and Thermodynamics, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria; stylianos.flegkas@tuwien.ac.at
²) RHI AG, Magnesitstraße 2, 8700 Leoben, Austria
³) Institute of Chemical Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria
⁴) Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

Abstract

The development of novel thermal energy storage concepts is of great importance to achieve the shift towards sustainable energy systems. Due to the volatile nature of renewable energy resources the interest in storage methods in order to match the intermittent output with customer demand has increased rapidly. Thermochemical energy storage is a very promising alternative to latent and sensible thermal energy storage systems, mainly because of the high energy density per volume and the possibility of nearly loss-free storage at ambient temperature.

In this paper a concept utilizing solid-gas reactions and a cascaded system of fluidized bed reactors for waste-heat recovery of gas compressor stations is presented. Due to the isothermal operation of reactor, it is not possible to cool the heat source beyond the temperature level that is defined by the storage material. Therefore, it is advantageous to use a combination of materials to obtain high heat-recovery effectiveness and minimize exergy losses.

Kinetic and equilibrium models for the reactors are used in order to determine the temperature levels of energy storage and release. The mass and energy balances are solved to obtain the required amount of the storage material and to calculate the mass-flow and the temperature of the fluidization gas. Also all peripheral systems (fluidization gas compressors, heat exchangers and pumps) are taken into account for an energy assessment.

Two variants of a heat storage process are proposed. The first variant uses a configuration where only the heat from the fluidization gas is recovered. The second variant includes a fluidized bed recuperator to recover the heat from the produced solid mass stream. It is concluded that by recovering the heat from the particles that exit the reactors and using it to heat up the entering solid stream, a heat output increase of 34.8% is achieved.

1. Introduction

Considering the ever increasing energy demand in combination with the trend towards sustainable energy sources, innovative energy storage concepts are required to compensate the fluctuating supply and meet consumer demand. Amongst the existing thermal energy storage technologies, thermochemical energy storage (TCES) is very promising compared to sensible or latent heat storage concepts. The concept is based on a reversible reaction system where heat is absorbed in an endothermic decomposition reaction. That way the heat can be stored indefinitely at ambient conditions until it is released by initiating the reverse reaction. The main advantages of TCES have been summed up by Pardo et al and André et al. [1, 2]: nearly loss-free storage at ambient temperature, transportability and high volumetric energy density ($500 \text{ kWh/m}^3$) compared to latent ($100 \text{ kWh/m}^3$) and sensible ($50 \text{ kWh/m}^3$) heat storage.

Potential applications of a TCES system for heat recovery are gas compressor stations. A study on waste heat recovery from these stations was performed by Campana et al [3]. They stations are used to maintain the gas pressure in natural gas pipelines. Typically a gas turbine that is fuelled by a portion of the transported gas stream is used to drive a compressor. The exhaust gases are available at temperature levels above 645K. It was estimated by Tavakkoli et al [4], that their heat recovery potential in the USA is on average 610TJ/day. At the moment this heat is not utilized, because these compressor stations are located at very remote locations, where no demand exists. The transportability of TCM would allow the transfer of heat to other sites, where it can be utilized.

Regarding reactor concepts, fixed bed, moving bed as well as fluidized bed reactors have been considered and
compared by Solé et al. [5] for TCES applications. The properties of the latter are described by Kunii and Levenspiel [6]. They offer high heat and mass transfer rates, isothermal operating conditions and high heat transfer coefficients and are therefore preferred for this application. The downside of this reactor concept is, that it does not permit to cool the heat source below the turning temperature of the TCM.

This means that if a material with a high turning point is chosen, the temperature interval up to ambient temperature would not be utilized, while a material with a lower turning point would lead to significant exergy losses. In this paper an approach to overcome this drawback is proposed: A series of fluidized bed reactors with different storage materials are arranged in a cascade to efficiently utilize the waste heat source.

2. Theoretical background

2.1. Reaction selection

A vast number of potential reversible solid-gas reactions that are suited for TCES have been presented by Deutsch et al. [7]. From these candidates, three reaction pairs with different turning temperatures were chosen for the simulation: Calcium oxide / calcium hydroxide, magnesium oxide/magnesium hydroxide and calcium oxalate/calcium oxalate monohydrate.

An extensively studied reaction system for high temperature storage is the hydration and dehydration reaction of calcium oxide/calcium hydroxide:

$$\text{CaO} (s) + \text{H}_2\text{O} (g) \rightleftharpoons \text{Ca(OH)}_2 (s)$$

$$\Delta H_r = -104 \text{ kJ/mol} \quad (1)$$

For this system correlations for the reaction kinetics have been proposed by Schaube et al. as well as Criado et al. [8,9]. Also the applicability in fixed bed reactors has been shown proved by Yan et al. and Schmidt et al. [10,11] as well as in fluidized bed reactors by Pardo et al. [12].

For the intermediate temperature level, the reaction system magnesium oxide/ magnesium hydroxide was chosen:

$$\text{MgO} (s) + \text{H}_2\text{O} (g) \rightleftharpoons \text{Mg(OH)}_2 (s)$$

$$\Delta H_r = -81 \text{ kJ/mol} \quad (2)$$

This system was considered by Kato et al. [13,14] for an application in a chemical heat pump. The kinetics of this reaction system were also investigated by Pan et al. [15] while Widhalm et al. [16] performed an in depth energetic end economic analysis of a district heating concept utilizing this reaction pair.

Recently the calcium oxalate/calcium oxalate monohydrate system was proposed as a low temperature TCM:

$$\text{CaC}_2\text{O}_4 (s) + \text{H}_2\text{O} (g) \rightleftharpoons \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} (s)$$

$$\Delta H_r = -6.7 \text{ kJ/mol} \quad (3)$$

Knoll et al. [17] tested the cycle stability of the material and showed that even after 100 cycles no deviation in terms of reaction rate, mass change and heat flow is observed. The kinetics of the dehydration reaction have been studied by many authors, an overview is given by Vlaev et al. [18]. Kinetic models for the hydration reaction are not available in literature, hence an equilibrium model was chosen to describe this reaction.

2.2. Reactor modelling

The conversion rate of solid-gas reactions is described by Vyazovkin et al. [19] on the basis of three variables: The temperature $T$ at which the reaction occurs, the extent of conversion $\alpha$ and the partial pressure of the gaseous reactant $p$ as follows:

$$\frac{da}{dt} = k(T) f(\alpha) h(p) \quad (4)$$

The temperature dependency $k(T)$ is described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where $A$ is the pre-exponential factor, $E_a$ the activation energy of the reaction and $R$ the universal gas constant.

The conversion progression is described by a reaction model $f(\alpha)$ or $g(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)}$ in integrated form. Galwey et al. [20] provide an overview of reaction models for solid state kinetics and their theoretical background.

The kinetics of hydration and dehydration also depend on the partial pressure of the steam in the fluidization gas. Since most of the relevant reactions follow a simple stoichiometry the partial pressure dependency is described in relation to the equilibrium pressure $p_{eq}$ as [8]:

$$h(p) = \left(\frac{p}{p_{eq}} - 1\right)^\nu \quad (6)$$

where $\nu$ is an empirical exponent. Consequently the integration of Equation (4) yields:

$$\int_{\alpha_{in}}^{\alpha_{out}} \frac{da}{f(\alpha)} = \int_0^\tau A \exp\left(-\frac{E_a}{RT}\right) h(p) \, dt \quad (7)$$
It is assumed that the material enters the reactor at \( t = 0 \) with an initial degree of conversion \( \alpha_{in} \). The assumption of isothermal and isobaric conditions inside the fluidized bed reactor leads to an analytical solution.

\[
g(\alpha_{out}) - g(\alpha_{in}) = A \exp \left( - \frac{E_a}{RT} \right) h(p) \tau
\]  
(8)

The mean residence time \( \tau \) of the solids inside the reactor is defined as:

\[
\tau = \frac{M}{\dot{m}_{s,in}}
\]  
(9)

where \( M \) is the mass of the solids inside the reactor.

Generally individual particles do not have the same residence time in a continuously operating fluidized bed reactor. Kunii and Levenspiel [6] proposed a modification of Equation (8) that takes the residence time distribution \( E(t) \) into account, yielding the final conversion of the exiting solid stream \( \alpha_{FBR} \):

\[
1 - \alpha_{FBR} = \int_0^\infty (1 - \alpha_{out}) E(t) dt
\]  
(10)

Since the reactors are operating with a constant feed rate of the solid reactant (subscript \( s \)) and gas (subscript \( g \)) the mass balance is given as:

\[
\dot{m}_{s,in} - \dot{m}_{s,out} + \dot{m}_{g,in} - \dot{m}_{g,out} = 0
\]  
(11)

During dehydration the released water from the reaction is carried out of the reactor by the fluidization gas. The molar flow of the produced materials is given by:

\[
\dot{n}_{o,out} = \dot{n}_{o,in} + \dot{n}_{OH,OH,in}
\]  
(12)

where the subscript \( O \) stands for oxide and \( OH \) for hydroxide. The energy balance of the reactor includes the enthalpy flows of the solid \( \Delta H_s \) and gas \( \Delta H_g \) streams, the heat transfer to the reactor bed from the in-bed heat exchanger surface \( \dot{Q}_{hex} \) and the heat absorbed by the reaction \( \dot{Q}_r \).

\[
\Delta H_s + \Delta H_g + \dot{Q}_r + \dot{Q}_{hex} = 0
\]  
(13)

2.3. System performance

For the evaluation of the systems performance the round trip efficiency \( \eta_{rt} \) of the system is defined as the ratio between the heat released by the exothermic reaction during the heat recovery process \( Q_{out} \) and the heat provided by the waste heat source \( Q_{wh} \).

\[
\eta_{rt} = \frac{Q_{out}}{Q_{wh}}
\]  
(14)

The compressor power consumption is a major cost factor for any process utilizing fluidized bed reactors. It is therefore crucial to estimate the power consumption, because if it is too high it might even outweigh the advantages of this reactor type. Assuming ideal gas behaviour the shaft work for adiabatic compression \( w \) is given by:

\[
w = \frac{k}{k-1} \eta_{comp} \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - 1
\]  
(15)

Here \( v_1 \) is the volumetric flow rate of the gas, \( k \) the heat capacity ratio, \( p_1 \) and \( p_2 \) the pressure before and after compression respectively and \( \eta_{comp} \) the compressor efficiency.

3. Concept and simulation

Fluidized bed reactors operate isothermally. This behaviour is useful for TCES applications because the temperature can be chosen so that the reaction takes place under optimal conditions. On the other hand, when utilizing a heat source for waste heat recovery, the goal is to cool the source as much as possible to achieve high heat recovery effectiveness. This means that the utilization of only one reaction system, would either not allow the effective utilization of the heat source, if the system reacts at high temperature values, or that the high temperature heat is downgraded, if a system reacting at low temperature levels is used.

The temperature level of flue gases from gas compressor stations is assumed to be 600°C. If only a high temperature storage system like Ca(OH)_2/CaO with a turning temperature of 515°C [2] was used, the temperature range below 515°C would remain unused. Another approach could be to use a reaction system with a lower turning temperature like Mg(OH)_2/MgO. In this case it would be possible to cool the heat source to the turning temperature of 265°C [2]. Yet this would mean that the heat could only be recovered at a much lower level than the original heat source resulting in high exergy losses.

Hence, in this paper an approach utilizing three reaction systems in a cascaded arrangement is proposed. This allows the efficient utilization of the waste heat source through TCES. Two variations of the process have been investigated and compared in terms of heat output, round trip efficiency and power input. For the different variants of the process, the final conversion of the TCM was set to 80%. This value has been chosen as it was shown to be an achievable conversion level without exceeding realistic residence times. From the resulting residence time the mass flow is calculated according to Equation (9). Also each storage reactor is provided the same amount of heat from the source in both variants.
Figure 1. Schematic of the distribution of the available waste heat

Figure 2. Process diagram of the $Ca(OH)_2/CaO$ stage of variant 1

Figure 1 illustrates the amount of heat that is transferred to the fluidized bed reactors from the heat source. Approximately $3.1 \, MW_{th}$ are transferred to the $Ca(OH)_2/CaO$ and $4.9 \, MW_{th}$ to the $Mg(OH)_2/MgO$ reactor. The heat source is further cooled down to $200^\circ C$ by the $CaC_2O_4 \cdot H_2O/CaC_2O_4$ reactor. A portion of the remaining heat is used in variants 2 and 3 to preheat the $CaC_2O_4 \cdot H_2O$ before it enters the last stage of the cascade. Overall $10 \, MW_{th}$ are supplied to the heat storage process in variant 1 and $10,6 \, MW_{th}$ in variant 2 respectively by the heat source.

All simulations were performed with gPROMS® ModelBuilder version 4.1.0 by Process Systems Enterprise (PSE).

3.1. Variant 1: Process with gas-recuperator

The first configuration consists of the fluidized bed reactor, a fluidization gas recuperator and a condenser. The same arrangement is used in all 3 stages of the cascade. Figure 2 illustrates the first stage (dehydration of $Ca(OH)_2$) of the energy storage process.

The water that is released during the endothermic reaction is transported out of the reactor by the fluidization gas and is subsequently condensed. The dry gas stream is heated in the recuperator so that it enters the reactor close to the reaction temperature level. The TCM enters the reactor at ambient temperature, where
it is heated up to the reaction temperature and is eventually converted. The sensible heat of the particles exiting the reactor is not recovered. The converted material is transported to another location for the heat release process. A flow diagram showing the mass flow within the reactor stage is depicted in Figure 3. It is obvious that because of the water released by the reaction, the exiting TCM mass-flow is smaller than the input.

The main losses of this process occur at the condenser, where the water that is released by the reaction is removed from the gas stream, and the unrecovered sensible heat of the exiting solid stream. Assuming that the fluidization gas-stream containing the released water is cooled to ambient temperature in order to condense and remove the water, approximately \(1,3 \, MW_{th}\) are lost to the surrounding. Additionally, the wasted sensible heat in the exiting solid-stream amounts to \(0,7 \, MW_{th}\). Considering that the heat exchanger provides about \(3,3 \, MW_{th}\) to the system, it is evident that the internal utilization of these losses would enhance the efficiency of the energy storage process.

The advantages of this configuration are its simplicity and the availability of all components. In the following variant an attempt was made to utilize these losses internally to improve the process efficiency.

3.2. Variant 2: Process with gas and solid-recuperator

In order to improve the process, the sensible heat of the exiting solid mass stream is utilized. From the energy balance it can be derived that the temperature at which the TCM enters the reactor has a significant impact on the reactor performance. It would be optimal for the solids to enter the reactor as close as possible to the reactor temperature but below a temperature level at which the reaction initiates.

In a fluidized bed recuperator, such as the concept proposed by Schwaiger et al. [21], two coupled fluidized beds are used to transfer the heat from the exiting particle stream to the entering particle stream to preheat the material. The solids are further heated by the hot fluidization gas that exits the reactor to reach a higher temperature level. This leads to a reduction of the residence time required for the TCM to reach a conversion level of 80% that has been defined for the comparison. This can be attributed to the fact that the solids do not have to be heated up to the reaction temperature inside the reactor by the heat source.

The flowsheet of the \(Ca(OH)_2/CaO\) reactor stage of variant 2 is depicted in Figure 4. Also, to further utilize the heat source, it is used to heat the \(CaC_2O_4\cdot H_2O/CaC_2O_4\) mixture that enters the last reactor stage.

![Figure 3. Mass-flow diagram of the dehydration stage of \(Ca(OH)_2\) in variant 1](image-url)
Additionally the heat of the fluidization gas is used to further increase the solid temperature. The hot gas stream is also utilized in the gas-gas heat exchanger to heat the fluidization gas, hence the cooling temperature is set to 350°C for the pre-heating of the TCM. The maximum achievable reactor inlet temperature of the solids using this configuration is 351°C (Figure 5).

The implementation of the pre-heating of solids leads to a more effective utilization of the heat source. Compared to variant 1 this configuration increases the output of the converted TCM stream by 32%.
4. Concept evaluation and discussion

The two variants proposed for waste heat utilization differ in terms of complexity and efficiency. In order to present an objective comparison, the produced TCM for the reheating process is compared. The produced \( Ca(OH)_2/CaO \) and \( Mg(OH)_2/MgO \) mixture increases from variant 1 to 2, due to the additional utilization of the heat source to pre-heat the TCM. When the particles enter the reactor heated-up, less time is required before they reach the reaction temperature. Hence the mean particle residence time in the reactors is reduced, resulting in a higher TCM production rate than in variant 1. The produced TCM streams of the different stages of all variants are illustrated in Figure 6.

Although a detailed design of a heat recovery process for the produced materials is beyond the scope of this paper, the recovered heat is taken into account for the energy assessment. It is assumed that a conversion level of 80% is achieved in the heat recovery process for all materials. The values of the converted mass flows are then multiplied with the reaction enthalpy to obtain the produced heat.

The amount of recoverable heat depends strongly on the heat release process. Issues like the supply of steam on the heat recovery site and the reheating of the TCM to reaction temperature, cause considerable losses and thus have a big impact on the heat recovery efficiency. An extensive discussion on how these parameters influence the feasibility of TCES systems is given by Flegkas et al [22]. Here an ideal recovery process is assumed for the sake of simplicity since the goal is only the comparison of the presented variants. Also any factor would affect each variant equally. Figure 7 illustrates the amount of heat that is released from the proposed variants under these assumptions, along with the maximum round trip efficiency.

For further assessment, the power requirement of all peripheral units in the proposed variants is compared. The compressor efficiency is assumed to be 70%. The fluidization velocity of the fluidized bed reactors is set between 2-3 times the minimum fluidization velocity in order to optimize the parameters relevant for the reaction. Additionally, it is beneficial to operate the fluidized bed recuperator at fluidization velocities slightly above the minimum fluidization velocity just in order to initiate the fluidized bed state. The results of the assessment are summed up in Table 1. The additional power consumption (7,7%) required for variant 2 compared to variant 1 leads to a significant heat output increase (34,8%) because of the utilization of the sensible heat of the converted TCM.

5. Conclusion

An approach to efficiently utilize high temperature waste heat in a cascaded TCES process has been proposed. Two variants that make use of the same reaction systems (magnesium oxide/magnesium hydroxide, calcium oxide/calcium hydroxide and calcium oxalate/calcium oxalate monohydrate) but differ in terms of complexity and efficiency were investigated.

![Figure 6. Comparison of the produced TCM streams](image-url)
The first variant consists of a simple system where the heat from the gas that exits the reactor is recovered to pre-heat the fluidization gas. In variant 2 the sensible heat from the converted solid stream is utilized by a fluidized bed recuperator to heat the entering unconverted solid stream, thereby enhancing the reactor performance. It was shown that the pre-heating of solids has a great impact on the performance of the process. The round trip efficiency of an ideal process is increased from 61.04% (variant 1) to 82.30% (variant 2) at an increased power consumption of the peripheral systems of 7.7%.

The process could be further improved by the additional utilization of the steam that is a product of the decomposition reaction thus avoiding condensation loses. Also the heat source could be utilized more efficiently by adding another reaction stage below the low temperature stage.

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References


