Heat transformation based on $CaCl_2/H_2O$ – Part B: open operation principle

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Abstract

In order to increase the efficiency of industrial processes by means of thermal energy storage and upgrade of waste heat in a temperature range of 100 °C - 200 °C thermochemical systems are a promising option. The working pair $CaCl_2/H_2O$ has been identified as suitable reference system due to the possibility to store thermal energy and perform an upgrade of thermal energy at the same time. As working principle an open mode with air as purge gas is investigated in this work. Thus, an operation at ambient pressure level as well as a less complex experimental setup can be realized. Therefore, a test facility has been set up for experimental investigation of the thermochemical system focusing on dehydration reaction. First, various reactor modifications are examined with respect to influence the pressure drop of the reactor containing the $CaCl_2$. It was shown that by the insertion of gas channels made of fine metal mesh a reduction of the pressure drop by factor 6 is possible in comparison to the unmodified fixed bed. Additionally, parametric studies have been carried out regarding the variation of charging temperature and volume rate of air. In order to obtain a high temperature lift in the heat transformation process, low thermal charging temperatures are targeted.

Nomenclature

Symbols

ΔH_R	enthalpy of reaction (J mol^{-1})	
m	mass (g)	
M	molar weight (g mol^{-1})	
p	pressure (kPa)	
p^0	Standard pressure (1 kPa)	
Δp	pressure drop (kPa)	
R	universal gas constant (J mol^{-1} K^{-1})	
t	time (min)	
$t_{X=90}$	time to 90 % overall conversion (min)	
T	temperature (°C)	
T^0	standard temperature (298 K)	
$\dot{V}$	volume flow (m^3 h^{-1})	
x	water vapor concentration (-)	
X	conversion (-)	

4   1. Introduction

5   In order to decrease CO_2 emissions in the industrial sector, an efficient use of energy is
6   necessary. Comparing the total energy consumption of Germany, a percentage of 29 % is
7   used for industrial purposes, while 64 % of this are used for thermal process heat supply [1].
8   Studies have shown that there are huge amounts of industrial waste heat with a temperature
9   level up to 150 °C [2]. Thus, a big potential for reducing costs and increasing efficiencies
10 exists in this sector. However, there are different process related reasons why a reutilization
11 of industrial waste heat seems currently not economical: Firstly, the temperature level of
12 waste heat doesn't satisfy process requirements for further utilization. Secondly, heat supply
13 and demand are poorly synchronized. To overcome these problems there are several
14 opportunities available. One approach is to store the waste heat in thermal energy storages
15 and release it at a time with higher heat demand. Furthermore, a continuous upgrade of
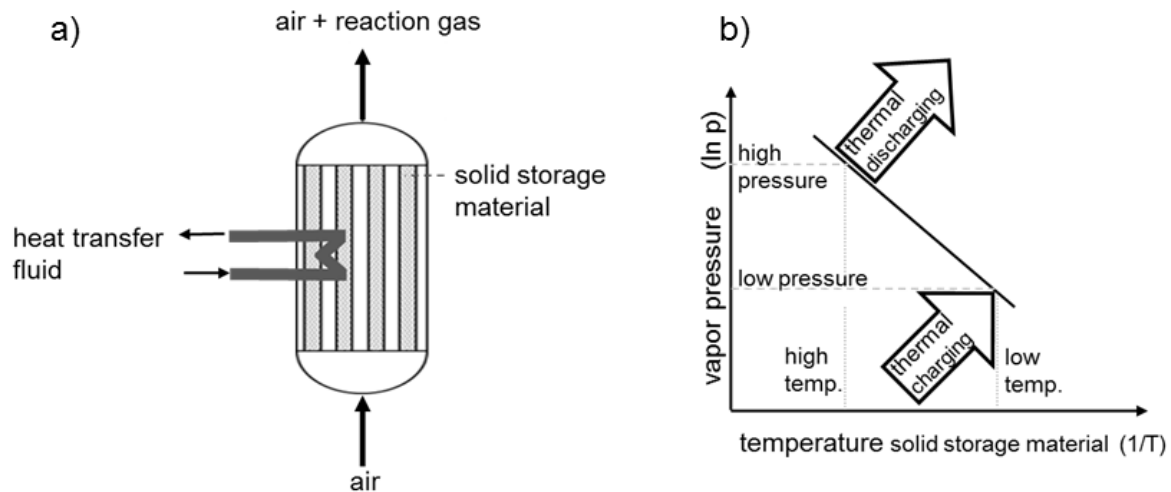16 waste heat to higher temperature levels can be performed using heat pumps.

17 In order to combine these options of thermal energy storage and upgrading waste heat,
18 thermochemical systems are a promising approach. Thermochemical systems are based on
19 reversible chemical reactions between two components. The charging process takes place
20 by thermal separation of the two components (endothermic). Release of heat occurs during
21 the reverse (exothermic) recombination reaction of the components. In general, the reaction
22 equation can be written as:

$$AB + \Delta H_R \rightleftharpoons A + B \qquad\qquad (1)$$
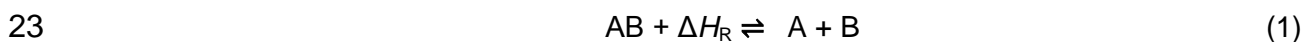
24 Thermochemical energy storage with gas-solid-reactions theoretically exhibit the advantage
25 of high volumetric energy storage densities and reduced heat losses during storage period.
26 Additionally, thermochemical systems offer the option to upgrade low temperature heat to
27 higher temperatures which is the main aspect of this paper.
28
29 The working principle of this kind of heat transformation can be described by the van't Hoff
30 chart displayed in Fig. 1b. The equilibrium line represents the correlation of vapor pressure
31 with given reaction temperature. In thermodynamic equilibrium, the gas pressure rises with
32 increasing temperature. According to the van't Hoff chart, thermal charging at low
33 temperatures is possible if the gas pressure is kept at a low level as well. The reverse
34 process, thermal discharging, occurs at a higher pressure resulting in high output
35 temperatures. Therefore, the thermal upgrade is performed between endothermic and
36 exothermic reaction by change of gas pressure. This can refer to the absolute as well as to
37 partial gas pressure. If the reaction is conducted in a gas mixture, e.g. air, the fraction of the
38 reactive gas can be changed. Thus, the overall pressure could be equal to ambience which
39 simplifies the construction of the technical components.
40

a) air + reaction gas

solid storage material

heat transfer fluid

air

b)

vapor pressure (ln p)

thermal discharging

high pressure

low pressure

high temp.

thermal charging

low temp.

temperature solid storage material (1/T)

1

2 **Fig. 1 a)** Schematic of open system **b)** T/p-correlation (van't Hoff) - dependency of vapor pressure (reaction
3 gas) and equilibrium temperature (solid storage material)

4 For the purpose of performing a heat transformation with thermochemical systems an open
5 operation mode is a promising option. In this case, an inert gas (e.g. air) flows through the
6 reactor removing the reaction gas and releasing it to environment (see schematic in Fig. 1a.)
7 The gaseous reaction component needs to be environmentally friendly, e.g. water vapor.
8 Due to the reduced requirements (no vacuum, no additional storage container, no cold sink)
9 the open system is rather simple and consequently high storage densities on a system level
10 can be expected.

2. State of art and aim of work

12 In this chapter the state-of-the-art of thermochemical systems regarding heat transformation
13 of industrial waste heat is presented. Various systems are proposed able to upgrade waste
14 heat in a temperature range between 100 °C – 200 °C.

15 <u>Water / sorption</u>
16 Well known physical sorption systems are zeolites or silica gels using water as reaction gas.
17 Based on zeolite, a mobile thermal heat storage was built up by Krönauer et al. for waste
18 heat utilization from a incineration plant [4]. As operating principle an open system is used
19 with air as purge gas. Thermal charging takes place at a temperature level up to 130 °C by
20 means of dry air releasing the water steam to the environment. Extraction of thermal energy
21 occurs by the use of humid air generating output temperatures up to 150 °C.
22
23 <u>Ammonia</u>
24 P. Neveau et al. reported on different ammonia based working pairs suitable for a wide range
25 of temperatures [5]. Based on these data, Wongsuwan et al. suggested several ammonia-
26 salt systems as promising working pairs for upgrading waste heat with an appropriate
27 temperature lift [6]. Experimental studies were carried out by Haije et al. investigating the
28 performance of the ammonia-salt system $LiCl$-$MgCl_2$ / NH_3 for purposes of heat
29 transformation [7]. Li et al. proposing an improved sorption cycle and a theoretical analysis
30 with the ammonia-salt system $MnCl_2$-$CaCl_2$ / NH_3 for upgrading low thermal energy up to

3

171 °C [8]. However, due to strong toxicity of ammonia these reactions are only applicable in closed systems without any contact to ambient atmosphere.

#### Metal hydrides

Dantzer et al. proposed a selection of various metal-hydrides capable to react reversible with hydrogen as reaction gas [9]. A two stage metal hydride heat transformer was developed by Willers et al. upgrading thermal heat from a temperature level of 130 °C up to 200 °C [10]. Another system based on different metal hydrides is set up by Suda et al [11]. In order to perform a heat transformation a low grade thermal energy source of 80 °C is used to generate a high output temperature of about 120 °C for steam generating applications.

Water / Salt-Hydrates

In order to realize a thermal heat storage or in combination with the possibility to transform heat in the target temperature range of 100 °C − 200 °C water based thermochemical systems seem to be promising candidates. Water steam used as heat transfer fluid is widely spread in thermal industrial processes for heating purposes in various technical applications. Additionally, using water vapor as nontoxic medium, also an open system as operation principle (as proposed in this paper) is feasible since the reaction gas can be released to the environment. Up to now there are only a couple of water based salt hydrates experimental investigated regarding suitability for thermal upgrade of industrial waste heat. Studies about the working pair Na_2S-H_2O with respect to structure, thermodynamic and phase properties have been carried out by De Boer et al. [12]. In order to avoid the deliquescence of the solid material during regeneration, temperatures above 83 °C may not be exceeded. Thus suitability for higher temperatures within industrial processes was not given. For the utilization in a chemical heat pump the reaction pair $MnCl_2$ / H_2O is examined by Stitou et al. focusing on the reverse reaction between the anhydrate and the monohydrate [13]. Experimental results showed that a thermal upgrade from 95 °C to 160 °C during thermal discharging is achievable. However, thermal charging of the reaction systems needs around 320 °C.

In order to investigate the upgrade of industrial waste heat by means of an open process in the temperature range of 100 °C − 200 °C, the thermochemical system $CaCl_2$ / H_2O was chosen as reference material. The generic reaction equation is given in equation 2. However, the overall reaction is more complex since it occurs with intermediate steps. Details are reported by Molenda et al. [3].

$$CaCl_2 \cdot 2H_2O_{(s)} \rightleftharpoons CaCl_{2(s)} + 2H_2O_{(g)} \qquad (2)$$
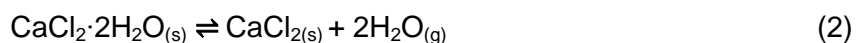
The present paper includes an experimental part with examinations using different reactor modifications for charging process analyzing their influence on the pressure drop. Additionally, parametric studies are conducted regarding charging temperatures and flow rate of purge gas. The results are analyzed with respect to pressure drop, conversion time and progress of fixed bed temperatures. The aim is to increase the potential thermal upgrade of the heat transformer by decreasing the charging temperature. The respective discharging experiments at different water vapor pressures are not part of this study but are being reported in the associated paper of Richter et al.

3. Experimental

3.1. Setup

For experimental investigations of the open operation of the thermochemical system a test facility was built up. The main component of the test bench represents the reactor designed as tube bundle heat exchanger. It consists of 31 tubes with a diameter of 9 mm each and a height of 400 mm surrounded by a shell. Within the tubes the solid granular $CaCl_2$ dihydrate is placed. Filters with a mesh size of 13 µm are installed at the in- and outlet of the tubes. The supply of air as purge gas is provided by the internal compressed air network. By means of an electric preheater, the air can be heated up to 200 °C. In order to measure the temperature within the packed bed, 10 thermocouples at different heights of the tubes are installed. Inserted through the bottom of the reactor, the thermocouples are placed every 66 mm. For the supply of thermal energy during dehydration process thermo-oil is used streaming through the shell-side of the reactor. The temperature of the thermo-oil can be adjusted by a thermostatic bath up to the maximum temperature of 200 °C. Due to the reactor design an indirect heat transfer via thermo-oil as well as a direct heat transfer by the heated air flow occurs. In order to receive information about the conversion of the reaction, a gas analyzer is installed. The gas analyzer measures the concentration of water vapor at the in- and outlet of the reactor. Additionally, pressure sensors are attached at the in- and outlet detecting the pressure drop of the reactor. To prevent condensation electric heating lines are installed at the piping of the test-bench as well as at the in- and outlet of the reactor.
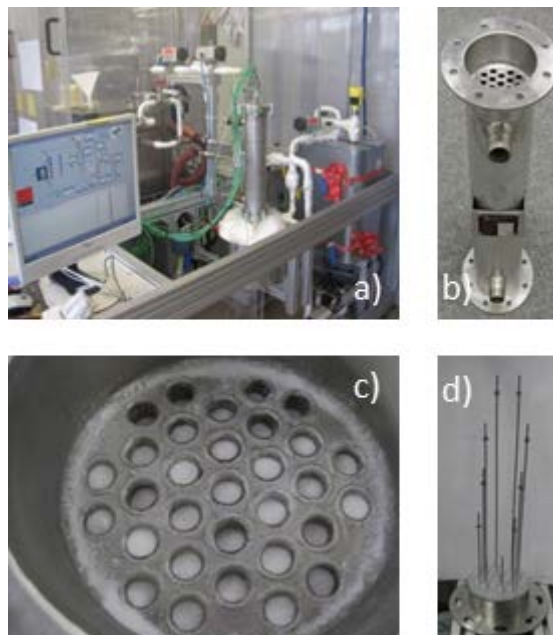
Fig. 2 a) Test facility, reactor **b)** tube bundle heat exchanger as reactor **c)** $CaCl_2$ packed bed in tubes
d) thermocouples for temperature measurements at different heights of packed bed

3.2. Procedure

Fresh material of calcium chloride dihydrate $CaCl_2 \cdot 2H_2O$ (Macco Organiques s.r.o) for every dehydration experiment is used. Two different operation modes are taken into account. The unmodified reaction bed and subsequently the modified reaction bed with gas channels were investigated. Before starting, the reactor is heated by the thermo-oil to experimental conditions. The air is heated by the electric preheater to charging temperature and streaming through a bypass. In order to initiate dehydration reaction, the dry and hot air flow is led

1   through the reaction bed. Due to the dehydration reaction water vapor is released increasing
2   the partial vapor pressure in the air. At the outlet of the reactor the gas mixture is analyzed.
3   By the use of the pressure sensors the pressure drop of the reaction bed is detected. A
4   parametric study of charging temperature and air volume flow is conducted, as shown in
5   Table 1.

|		volume flow	
		$4 \ m^3 \ h^{-1}$	$8 \ m^3 \ h^{-1}$
charging temperature	150 °C	um ; m	m
	130 °C	m	m
	100 °C		m

7   **Table 1**: Parameter variation of experiments (um: unmodified reaction bed; m: modified reaction bed)

8   4. Experimental results and discussion

9   4.1. Unmodified reaction bed

10   First experiments were performed using the tube bundle heat exchanger as reactor with an
11   unmodified fixed bed of reaction material within the tubes. The experiment is carried out with
12   a mass of 720 g of $CaCl_2$ dihydrate distributed equally within the reactor tubes.

13   First experimental investigation of decomposition reaction of $CaCl_2$ dihydrate in the open
14   system is carried out under following boundary conditions: charging temperature is set to
15   150 °C (thermo-oil + air) and air flow is adjusted to $4 \ m^3 \ h^{-1}$. The dehydration reaction is
16   initiated by opening the valves at the in- and outlet of the reactor, whereby preheated air
17   flows through the packed bed of reaction material. According to the van't Hoff chart of
18   $CaCl_2 \cdot 2H_2O$ [3], the equilibrium pressure at a temperature of 150 °C is around 40 kPa. The
19   water content (partial pressure) of the incoming air can be assumed as zero. As a
20   consequence, the $CaCl_2$ dihydrate is dissociated and the dry air dilutes the released water
21   vapor. Due to the endothermic dissociation the temperature of the fixed bed decreases.
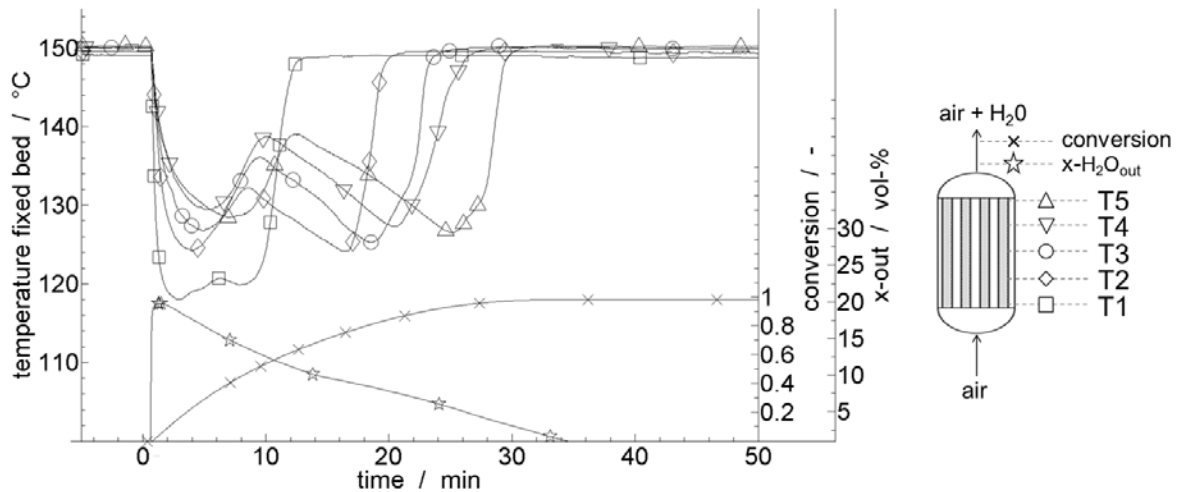
Fig. 3 Temperatures in the unmodified fixed bed, conversion, water vapor concentration at the outlet during dehydration reaction ($T_{dehyd} = 150\ °C$, $\dot{V} = 4\ m^3/h$)

As displayed in Fig. 3, at the inlet of the packed bed a temperature minimum is reached very quickly since at this position the lowest water vapor pressure is available. Along the fixed bed, the partial pressure of water vapor increases due to the dissociation reaction of the material. As a result of the decreased local temperature, a large temperature gradient to the tempered reactor wall occurs causing a high heat flux from the shell side of the reactor into the fixed bed. Due to these good reaction conditions (low water vapor pressure, large temperature difference) at the inlet a fast conversion is observed indicated by a fast return of local temperature to initial conditions of 150 °C. At sections of the fixed bed positioned along the axial axes the completion of dehydration reaction takes consequently longer due to the above mentioned continuous enrichment of the air stream with water vapor. According to Molenda et al [3], the decomposition of $CaCl_2$ dihydrate to anhydrous salt occurs in consecutive separate reactions steps. This reaction process explains the temperature evolution with two local minima representative for discrete reaction steps. First, the decomposition of $CaCl_2$ dihydrate to monohydrate takes place indicated by the temperature decrease to the first minimum of each temperature profile. After a short increase of the temperature, the second reaction step, the dissociation of monohydrate occurs and leads to the second local minimum. As soon as the anhydrous state is reached, the endothermic reaction is terminated which can be seen by the sharp increase of the respective temperature curve to its initial conditions. The completion of the dehydration process occurs with a plug flow behavior represented by the successive finalization of the reaction in local sections.

The concentration of water vapor released by the reaction is measured by a gas analyzer at the outlet of the reactor. At the beginning of the dehydration a peak of the water vapor concentration up to 20 Vol-% is measured (see Fig. 3). Afterwards a continuous drop is detected that occurs due to the termination of the decomposition reaction along with the formation of anhydrous $CaCl_2$ at sections close to the inlet. The slope of vapor concentration decreases at around t = 12 min. This behavior can be related to a completed conversion of the dihydrate phase, consequently from this point on only the monohydrate phase releases water vapor. Due to a lower equilibrium pressure of $CaCl_2$ monohydrate the driving force of

7

the reaction is reduced. Therefore, the decomposition is slow for the given boundary conditions. As soon as the entire decomposition is completed, the water vapor concentration at the outlet reaches again its original value of zero. In order to determine the overall conversion the measured water vapor concentration is used:

$$X_{\text{Conv.}} = \frac{m_{\text{H2O,out,exp}}}{m_{\text{H2O,tot,theo}}} = \dot{V}_{\text{air}} \cdot \int \frac{x_{\text{H2O,out}}}{1-x_{\text{H2O,out}}} \text{dt} \cdot \frac{p^0}{\text{R} \cdot T^0} \cdot \frac{M_{\text{CaCl2·2H2O}}}{2 \cdot m_{\text{CaCl2·2H2O}}} \cdot$$

(3)

As shown in the Fig. 3, the dehydration process reaches full conversion after around 30 – 35 min. During the experiment also the pressure drop of the purge gas through the entire reactor is measured by sensors attached at the in- and outlet of the reactor. In the unmodified fixed bed a very high pressure drop of $\Delta p = 62$ kPa is measured at a volume flow of 4 m^3/h. This pressure drop is related to the flow resistances of the particles as well as the filters at the in- and outlet of the reactor. In this context, especially the filter at the outlet is important since it prevents a discharge of reaction material by the gas flow. Due to the already high pressure drop and the limitations of the pressure sensors an increase of the air flow rate is not possible.

4.2. Modified reaction bed with gas channels

In order to reduce the pressure drop along the channels as well as to examine the influence of the air flow rate and charging temperature on the dehydration process, the set-up has been slightly modified. For this purpose gas channels made of fine metal mesh were designed (see Fig. 4a) and placed into the tubes of the reactor. The solid reaction material was inserted around the filter tubes (see Fig. 4b). Due to the gas channels the main part of the air volume flow does not flow through the whole cross-section of the fixed bed. Consequently, the pressure drop along the reaction bed should be clearly reduced. Although an exchange of water steam into the purge gas is possible, a penetration of single particles into gas channels can be prevented. The effect on the decomposition reaction is analyzed by subsequent experiments.
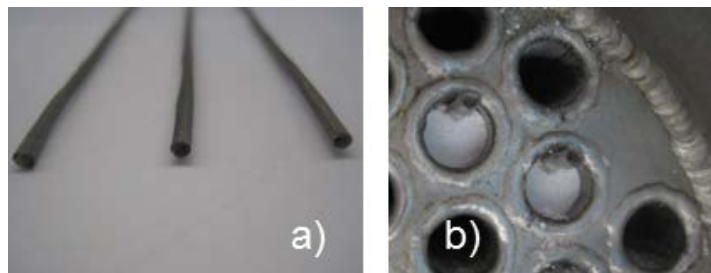
Fig. 4 a) Gas channels made of fine metal mesh (Ø ≈ 1 mm) **b)** Gas channels inside the packed bed of CaCl$_2$·2H$_2$O

Several experiments were carried out with charging temperatures to 150 °C, 130 °C and 100 °C and air flow rates of 4 m^3/h and 8 m^3/h, respectively. Due to the additional volume of the gas channels less space is available for the reaction material, thus for these experiments only approx. 630 g of CaCl$_2$·2H$_2$O were filled into the reactor.

During the experiments a significant improvement of the specific pressure drop in consequence of the installed gas channels was observed. As shown in Table 2 at a given charging temperature of 150 °C and a constant gas flow of 4 m^3/h, a reduction of the pressure drop by nearly a factor of 6 was reached. Thus, using the modification of the reaction bed, experiments with higher volume flow of purge air (8 m^3/h) are possible.

|		volume flow	
		4 m^3 h^{-1}	8 m^3 h^{-1}
charging temp. 150 °C	unmodified reaction bed	dp = 62 kPa	
	modified reaction bed	dp = 11 kPa	dp = 34 kPa

Table 2: Pressure drop of fixed bed influenced by reactor configuration and volume rate of purge gas

In the following the dehydration experiment with gas channels (T$_{dehyd}$ = 150 °C, $\dot{V}$ = 8 m^3/h) is presented in detail. In principle, the results displayed in Fig. 5 show a similar behavior compared to the experiments carried out with the unmodified fixed bed. According to the temperature evolution within the fixed bed, the completion of decomposition reaction also takes place by a plug flow behavior. Thereby, a reaction front moves from the inlet of the reactor to the outlet, indicated by the successive return of the respective local temperatures to external conditions of 150 °C. However, in comparison to the unmodified fixed bed, the temperature profiles are less defined. The differentiation of the two decomposition reaction steps is possible but less clear. Since the same effect occurs with a reduced gas flow of 4 m^3 h^{-1} (not shown), the influence of the higher gas flow can be excluded. One possible explanation could be based on the additionally required mass transfer process in radial direction - from the actual point of reaction to the channel. This would lead to an additional resistance and consequently to a less pronounced temperature drop due to the endothermic reaction.
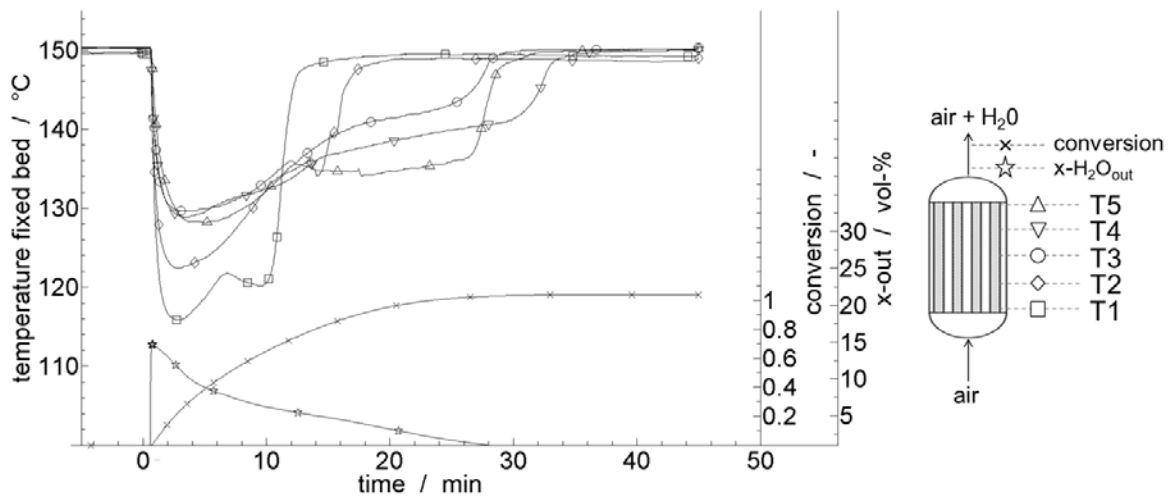
Fig. 5 Temperatures in the modified fixed bed (with gas channels), conversion, water steam concentration at the outlet during dehydration reaction (T_{dehyd} = 150 °C, $\dot{V}$ = 8 m³/h)

For the assessment of the dehydration performance, the time for 90 % of conversion is used ($t_{x=90}$). Fig. 6 shows the comparison of the dehydration performance for different temperatures and flow rates, respectively. A clear dependency between conversion time and charging temperature as well as air volume flow can be observed. The higher the charging temperature and the higher the volume flow the faster the reaction occurs. The rapid reaction can be explained by the high mass and heat transfer gradient between the reaction and the local boundaries during the reaction process. Additionally, due to the higher flow rates, a better dilution of the water vapor in the gaseous phase occurs, resulting in lower partial pressures. Therefore, with a flow rate of 8 m³/h, a dissociation of the reaction material is possible at an inlet temperature of 100 °C. Even though, this reaction is comparatively slow, it demonstrates that a charging of the reaction system is possible even at low temperatures.
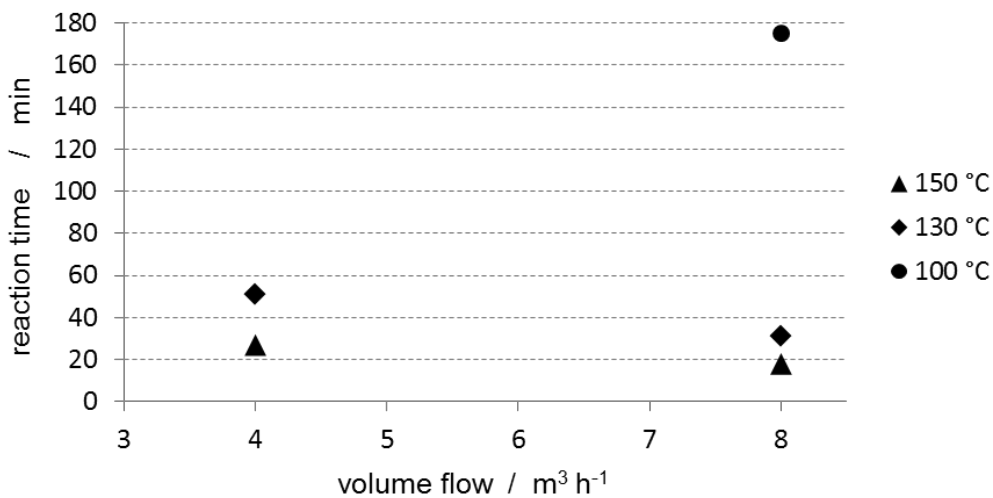
**Fig. 6** Conversion time ($t_{x=90}$) of dehydration in dependency of volume flow (air) at different charging temperatures

The influence of the charging temperature and the flow rate on the water vapor concentration measured at the outlet is shown in Fig. 7. For a given charging temperature the peak concentration at the beginning of the experiment is unaffected by the flow rate of the purge

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1 gas. However, with increasing reaction time, a higher flow rate leads to a faster decrease of
2 the outlet concentration and consequently to a faster conversion.
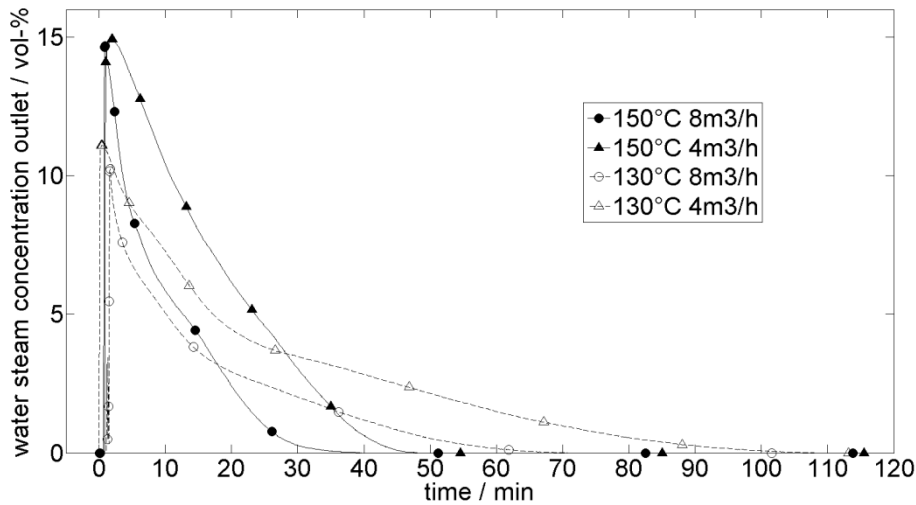
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4 **Fig. 7** Water vapor concentration at reactor outlet during dehydration at different experimental conditions

5 The impact of the temperature gradient between the reaction material (inlet of fixed bed) and
6 the reactor wall is shown in Fig. 8. The charging temperature T_{dehyd} is a boundary condition
7 (heated reactor wall) whereas the temperature of the reaction material at the inlet of the
8 reactor T_1 is a consequence of the reaction conditions. It is obvious that the largest gradient
9 occurs at the beginning of each experiment leading to a fast release of water vapor (compare
10 Fig. 8). Comparing the different charging temperatures, a correlation to the resulting
11 temperature gradient can be observed: the lower the charging temperature the smaller the
12 temperature gradient. This can be explained by the decrease in the rate of conversion for
13 lower charging temperatures.
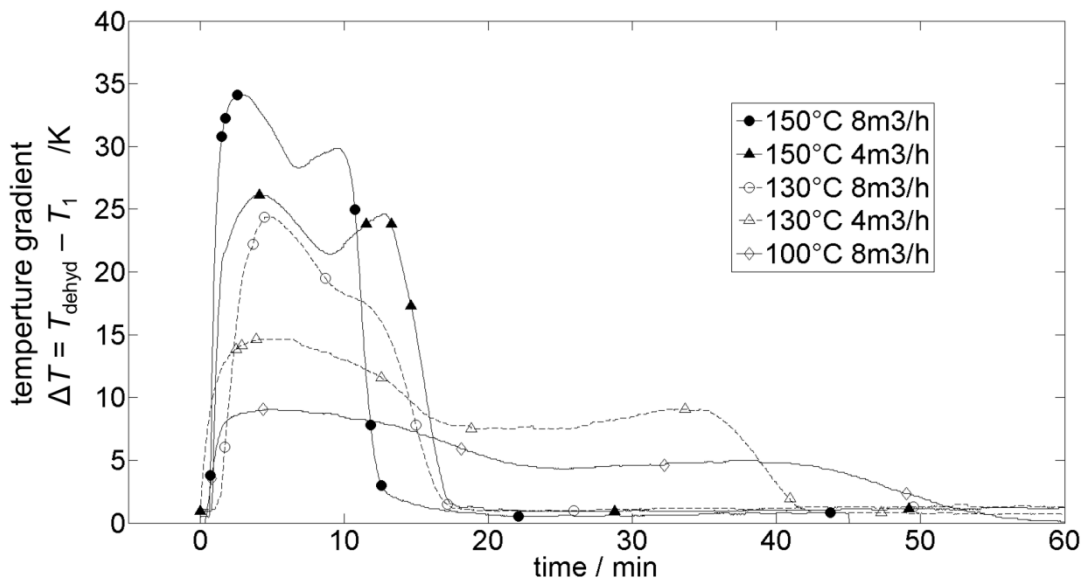
14

15 **Fig. 8** Temperature gradient between inlet of packed bed and tempered reactor wall (charging temp.) during
16 dehydration at different experimental conditions

11

With respect to the intended application of a thermal upgrade, one important purpose of the reaction is to reach high temperature lifts between the recovery of thermal energy and the thermal charging of the system. According to the associated paper of Richter et al., the discharging of the reaction system is possible at temperatures up to 165 °C using water vapor at atmospheric pressure. However, a trade-off between the power density of the reactor and the possible temperature lift of the heat transformer has to be faced.

5. Conclusions

Regarding waste heat recovery the reported open operation principle of a thermochemical system is very promising. It enables the utilization of waste heat at 100 °C. Waste heat at this temperature level is generally hard to integrate into industrial processes. However, applying the here presented open operation mode, this thermal energy could be used to charge a thermochemical storage. While the charging process is performed using dry air, discharging takes place at a vapor pressure of 100 kPa, as reported in the associated paper by Richter et al.. Thus, in an industrial application the thermochemical heat transformer is interesting especially if waste steam or waste heat at 100 °C (to generate steam) is available. Using the reference reaction system $CaCl_2/H_2O$ a thermal upgrade of approximately 65 K can be reached. If a maximum temperature lift is desired a long duration for the discharging needs to be accepted. From a technological point of view this might be questionable. Therefore, further work should focus on the effect of the intrinsic reaction kinetics on the reaction rate, new reaction materials as well as on possibilities to improve the heat transfer within the fixed bed.

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