Operation modes and process integration of a thermochemical heat storage system based on CaO/Ca(OH)$_2$
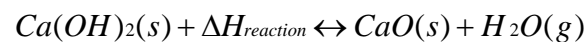
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1. Abstract

Efficient thermal energy storage systems for high temperatures at reasonable costs are essential for the economic success of concentrated solar power and can increase efficiency through the recovery of waste heat in industrial processes [1]. Due to the good availability at low cost and its favourable temperature range, previous work at DLR focused on the reversible dissociation reaction of calcium hydroxide:

$$Ca(OH)_2(s) + \Delta H_{reaction} \leftrightarrow CaO(s) + H_2O(g)$$

In order to investigate the reaction system, a multifunctional test bench as well as an indirectly operated reactor for 25kg Ca(OH)$_2$ was developed and put into operation at DLR [2]. Based on the performed experiments, the feasibility to store heat with the Ca(OH)$_2$/ CaO reaction system in a technically relevant scale (up to 10 kW) was demonstrated [3]. The dehydration was performed at 450 °C, while, during the hydration reaction with 1 bar water vapour, a reaction temperature of 500 °C was reached.

Besides necessary improvements in the conveyance of the material, integration concepts need to be developed, that allow an efficient operation of the thermal energy storage system. Consequently, the process parameters of the application system as well as possible operation modes of the thermochemical heat storage system must be understood. Particularly the incorporation of the reaction gas in the process is important to reach high overall cycle efficiencies. The partial use of low grade steam (100 °C) from the process, e. g. extracted from a steam turbine cycle, poses a possibility to drive the exothermic hydration reaction at 500°C. Nevertheless to evaluate the benefit of this thermal upgrade the overall application system needs to be taken into account.

This presentation will outline experimentally investigated operation characteristics of the Ca(OH)$_2$ heat storage reactor. Important parameters such as charge and discharge temperatures as well as the corresponding vapour pressures will be determined. An integration concept for a thermochemical storage system in a concentrated solar power plant is derived taking operating conditions of the plant and the storage system into account. Through modelling of the overall system, valuable results are obtained regarding the incorporation of the heat fluxes and the reaction gas as well as their influence on the overall cycle efficiency.

Keywords: thermochemical heat storage; moving bed reactor; operation modes

2. Introduction

In order to be able to realize large-scale energy storage system based on calcium hydroxide two crucial points need to be addressed:

First of all, it is necessary to decouple the power of the reactor from the capacity [4]. Based on this concept it is possible to store the material in cheap silo tanks and to minimize the reactor size with regard to the nominal power of the application. However, this concept implies the movement of the storage material through the reactor. The first part of this work therefore outlines an approach to improve the flowability of the fine powder material by dry coating. The modified material is investigated in a gravity-induced moving bed reactor under ambient conditions.

Secondly, an efficient integration of a calcium hydroxide storage system in processes with sensible heat transfer mediums is still outstanding. To develop process integration concepts the possible operation modes of the storage needs to be determined. The second part of this work therefore outlines experimentally determined parameters such as charge and discharge temperatures as well as the corresponding vapour pressures. Based on these results implications for the process integration are derived.

3. Development of a moving bed reactor

3.1 Material modification

In order to increase the powder flowability, two different approaches are possible. On one hand the particles can be pelletized to change the ratio of gravity force to Van-der-Waals force. In case of larger particles the gravity forces rise and the attraction between the pellets is minimized. Unfortunately, due to the volume change of the particles during the reaction these pellets break from cycle to cycle and a long-term stability has not been reached yet. On the other hand one approach is to increase the surface roughness of the single particles and thereby decreasing the Van-der-Waals forces. This can be reached by coating the surface with nanoparticles in order to reduce the contact area between two neighboured particles leading to a reduction of their adhesion forces.

In bulk industries several kinds of nanoparticles are known for minimizing the attraction forces [5]. They are mainly used as flowing agents for powders to improve their handling during processing. In case of thermochemical heat storages however, some more requirements are necessary. First of all, they have to resist high temperatures – in case of $Ca(OH)_2$ up to 600 °C. Secondly, they should not influence the thermochemical reaction, thirdly, steric stability on the surface must be given and last but not least they have to be offered at a low price to allow for a potential a large-scale application. Considering these conditions SiO_2, brand named Aerosil® by Evonik Industries, seems to be promising and is therefore used in this work.
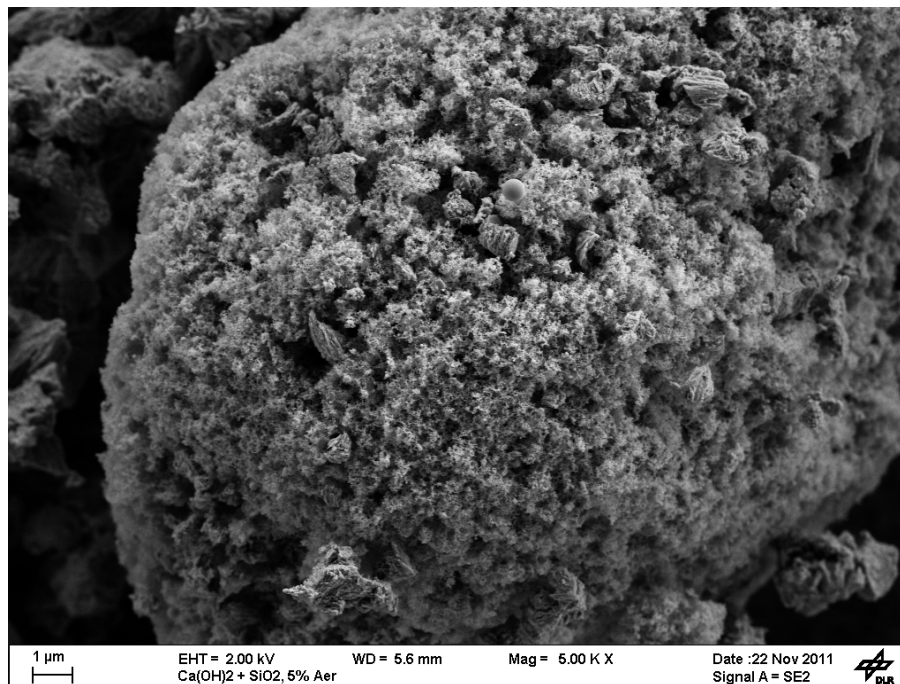
Figure 1 Ca(OH)$_2$ coated with 10 % Aerosil

Their primary particle size is 7 nm, the loss on ignition at 1000 °C is less than 2 w% and they are commonly used in food and drug industries as flow agents.

The substantial difference for the coating process in this case is the inorganic character and the fissured irregular shape of the Ca(OH)$_2$ particles. So, whereas amounts up to 1 w% are enough in 'conventional' bulk industries, an addition up to 10 w% is necessary for improving the powder flowability of Ca(OH)$_2$ at ambient temperature. Additionally, it is a complex interaction of mixing duration, intensity and quantity to be added during the dry mixing process of Ca(OH)$_2$ and SiO$_2$ nanoparticles. Thereby it is important to achieve a homogeneous coated layer on the host particles which can be proven by scanning electron microscopy (compare Figure 1). If the surface is well coated, the flowability can be improved so that a gravity induced flow in a moving bed reactor is feasible. After a quantitatively investigation of the powder flowability, the flow behaviour has to be studied in a thermochemical reactor including the chemical reaction.

3.2 Investigation of a gravity assisted moving bed reactor

Derived by the geometry of the fixed-bed reactor in pilot-plant scale (compare section 4) a moving bed reactor is designed in lab-scale. Figure 2 shows the set-up of the test bench. The reaction material is kept in a storage tank and moved to the moving bed reactor by a screw conveyor (green part) where the material can be heated up before entering the reaction zone. Afterwards the material flows through the thermochemical reactor (red part). In this section, the chemical reaction takes place.
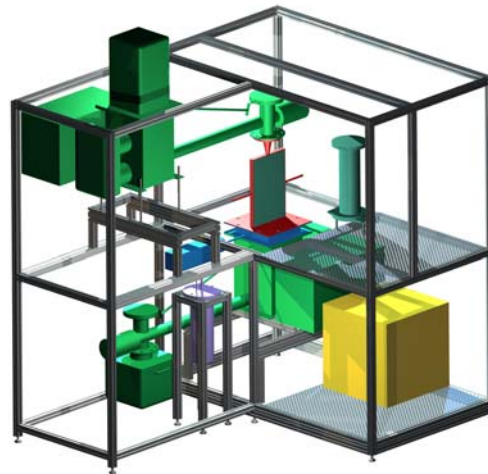
Figure 2 Test bench set up for moving bed reactor

The required water vapour is provided by an electrical heated pressurizer (purple part). During the dehydration of the material the reactor can be purged by a nitrogen flow. Air serves as heat transfer fluid and is preheated in an air heater (yellow part). After the thermochemical reaction the material is cooled down in another screw conveyor and stored in an additional tank. In order to study the flow behaviour at ambient conditions and to get an optical impression about the flow within the reaction zone gap, an acryl glass reactor has been integrated into the test-bench (compare Figure 3).

Figure 3 Test-bench with acryl glass reactor for moving bed reactor

The aim of this study was to investigate the flow behaviour of pure $Ca(OH)_2$ and to compare it with the modified one. Therefore, the reactor was filled with powder by the upper conveyor. As soon as a certain filling level was reached the lower screw conveyor was turned on and continuous operating mode was adjusted. Figure 4 shows the results of the experiments with pure $Ca(OH)_2$ (left) and with $Ca(OH)_2$ with the addition of 10 w% Aerosil (right).
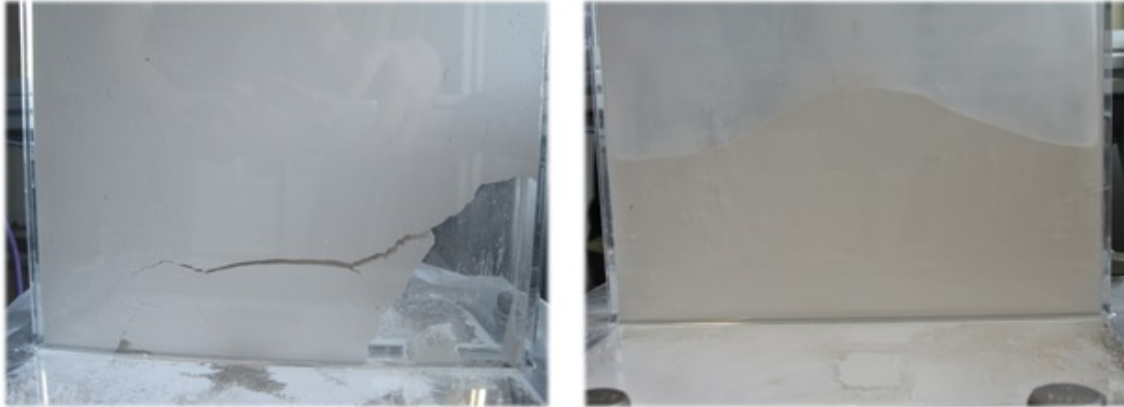

Figure 4 Flow behaviour of pure (left) and modified (right) CaOH)$_2$ in lab-scale reactor at ambient conditions

On the left picture of Figure 4, the flow behaviour of pure $Ca(OH)_2$ is shown. Here, bridging effects inhibit the homogeneous flow of the particles through the reactor. The powder bed stagnates and a constant movement of the bed is impossible. On the contrary, the powder modified with 10 w% Aerosil shows no bridging effects and a homogeneous flow can be realized.

In summary, a moving bed at ambient conditions can be realized by the addition of free flowing agents. Aerosils seem suitable to improve the flowability and can resist high temperatures. However, an adequate flow characteristic depends on complex interactions of mixing parameters. The next step will be the investigation of the flow behaviour during chemical reaction. Here, further influences like gas flow, volume change of particles and hot temperatures have to be studied.

4. Determination of operation modes

4.1 Experimental set up

Parallel to the investigations of the moving bed reactor at ambient conditions, possible operation modes of the calcium hydroxide material system are determined with a stationary bed reactor. The indirect plate heat exchanger design is shown in Figure 5.
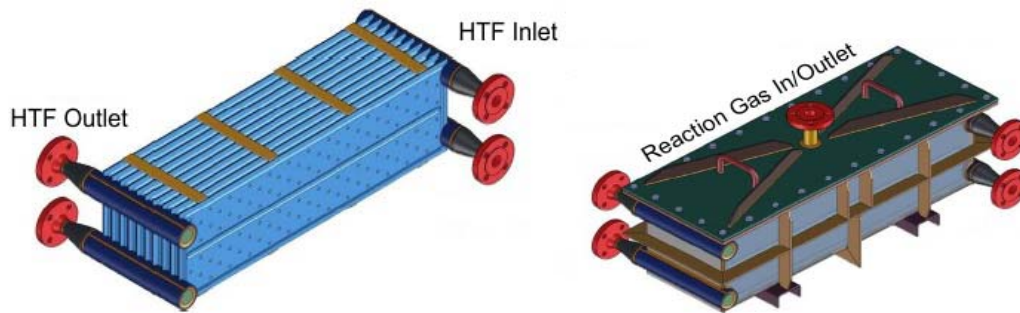
Figure 5 Indirect bed reactor for 25kg calcium hydroxide

The reaction material is filled in ten 20 mm wide and 250 mm deep channels between the heat exchanger plates. Air, serving as the HTF, steams inside these special thermo shelves thereby delivering or taking up heat to or from the reaction bed. The reaction gas enters or leaves the reactor through the flange connection in the centre of the cover (Figure 5 right). This cross flow arrangement ensures a uniform gas distribution within the whole reaction bed.

4.2   Experimental methodology

Figure 6 shows the equilibrium line of the calcium hydroxide reaction system, which characterizes the correlation between the partial pressure of the reaction gas and the temperature of the reaction. In order to understand the operation principle of the thermochemical storage reactor a detailed understanding of the equilibrium line is necessary.

For instance, at point one calcium hydroxide at a temperature of 410°C and a present vapour pressure of 0,1 bar are in equilibrium state. If now heat is supplied at temperatures above 410°C and the vapour pressure is simultaneously kept constant the equilibrium shifts to the CaO side – thereby thermal energy is stored as chemical potential.
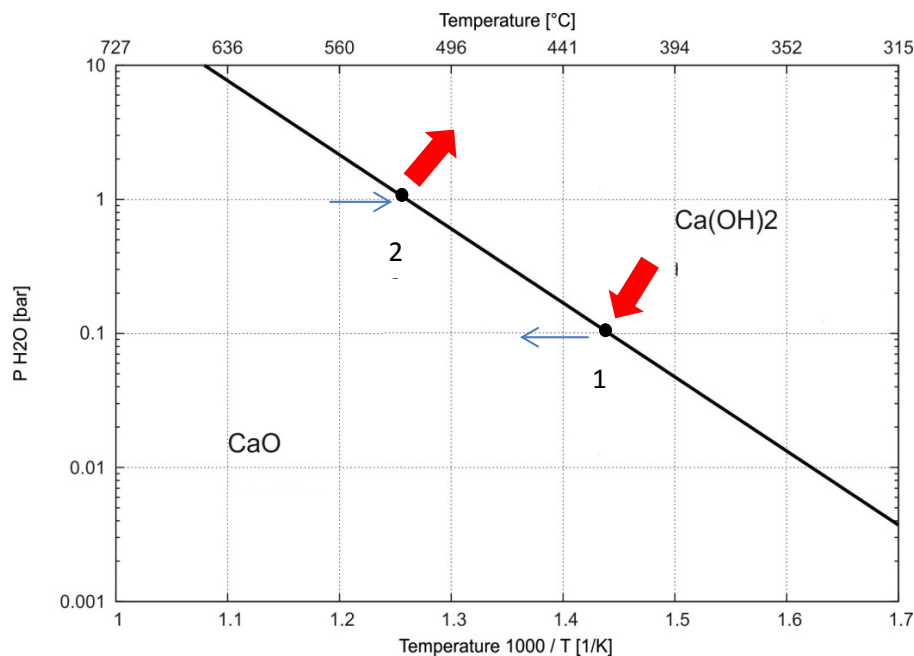

Figure 6 Equilibrium line of calcium hydroxide

During this charging mode of the storage reactor, excess heat available from a process can be used to drive the endothermal dehydration of calcium hydroxide to calcium oxide. According to the equilibrium line the dehydration at a low vapour pressure is favourable since the lower equilibrium temperature of the reaction extends the temperature range of the heat which can be incorporated. Therefore, a feasible operation point for the charging mode is currently considered at 0.1 bar vapour pressure and 410 °C (point 1 Figure 6). Lower vapour pressures are theoretically possible but required water vapour removal at very low pressures and demand additional sealing requirements.

During the discharging mode of the storage reactor, the exothermal hydration from CaO to $Ca(OH)_2$ takes place in the reactor and the heat of reaction should be taken up by the heat transfer fluid and delivered to the process. Depending on the temperature required by the process application the equilibrium temperature of the hydration reaction can be adjusted through the applied vapour (partial) pressure. In general, it is favourable if the hydration is performed at higher partial pressures than the dehydration. The operation point for the discharge of the storage reactor in this work is at 1 bar water vapour pressure (point 2 in Figure 6).

4.3 Experimental results - Charging mode

Figure 7 shows the temperature trend versus time for the charging process. T5, T11 and T13 are temperatures in the reaction bed along the flow direction of the heat transfer fluid. The green trend line is the vapour pressure measured before the reaction gas inlet flange of the reactor. At the beginning of the charging procedure the set-up is preheated to 300 °C, the condensation pressure in the condenser is set to 20 mbar.
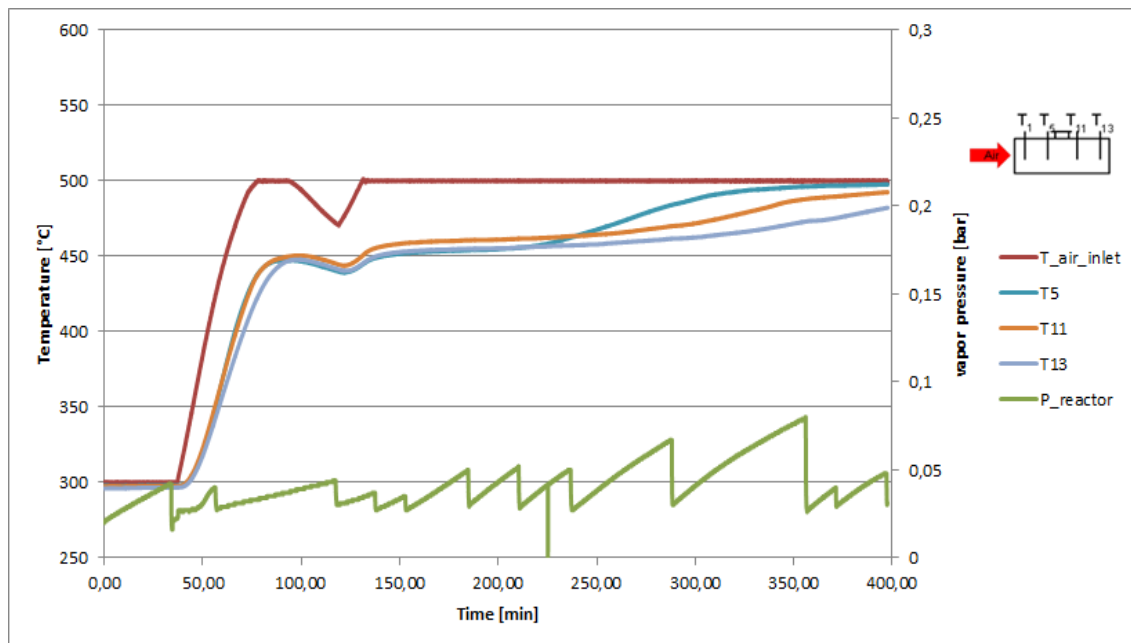

Figure 7 Temperature trend during charging mode

At minute 45 the air inlet temperature is set to 500 °C and the valve between the reactor and the condenser is opened. Until minute 70 the temperatures in the material bed increase with the same gradient as the air inlet temperature rises - indicating only sensible warming of the material. The initiation of the dehydration reaction is then clearly visible by the constant temperature plateau reached at 450 °C (minute 90). From that point on, the heat flux from the 500 °C hot air side to the material bed drives the endothermal dehydration of the calcium hydroxide. The constant equilibrium temperature indicates also a constant vapour pressure in

the reactor. The slight increase of the monitored pressure (compare green trend line in figure 7) is caused by small amounts of inert gases which are also freed during operation. These inert gases are removed out of the system by repeated connection of the vacuum pump. After 300 minutes the material in the reactor has completely converted to CaO and the material starts to increase its temperature again.

The charging of the storage reactor at constant temperature and reaction gas pressure were performed successfully. However, the equilibrium temperature during the experiment was 450 °C according to a vapour pressure of 0.32 bar even though the measured condensation pressure was 20 mbar. This effect is most likely caused by an increasing pressure drop along the reaction bed and the filter construction at low vapour pressures. Since the dehydration at a lower equilibrium temperature is important in order to enhance process integration efficiency this effect is currently investigated.

4.4 Experimental results - Discharging modes

During the discharging of the storage reactor the exothermal hydration reaction of CaO to $Ca(OH)_2$ is performed. Thereby, the discharge temperature of the storage can be adjusted by the vapour pressure. Within this work two different operation strategies for the discharge have been performed.
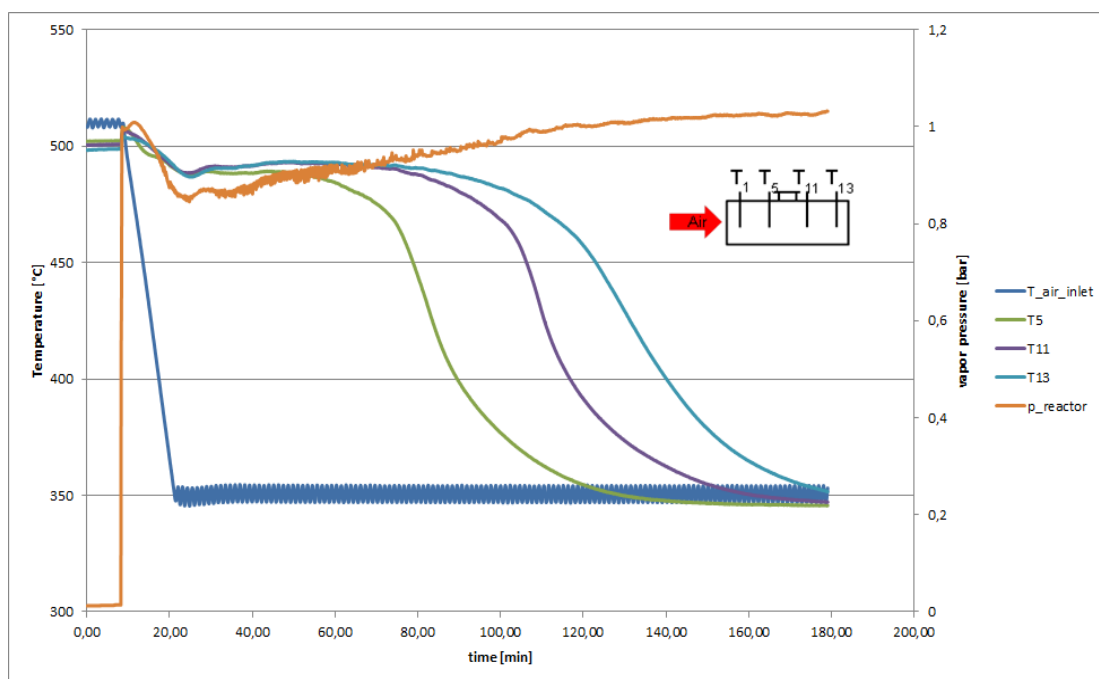

Figure 8 Temperature trend during discharge in buffer storage mode

In the buffer storage mode the storage system should supply additional thermal power to keep the process temperature constant in periods where the thermal power of a fluctuating heat source is insufficient. Figure 8 shows the temperature trend of the air and the storage material temperatures for this operation mode. Initially, the set-up was heated up to a steady state operation point at 500 °C. At minute 18 the air inlet temperature starts to decreases linearly to 350 °C thereby simulating a lack of thermal power. Simultaneously, the reactor is connected to an evaporator which supplies 1 bar water vapour. Consequently, the storage temperatures in the direction of the air flow T5, T11 and T13 remain constant at 490 °C indicating the ongoing exothermal hydration reaction. T5 starts to drop at minute 60 indicating that the material in this part of the reactor is already completely converted. In contrast, the temperature in the rear area of the reactor starts to decrease around minute 110 (compare T13).

Therefore, a temperature of 490 °C in the storage was hold for 50 minutes. The reached temperatures in the storage thereby corresponded to the applied vapour pressure of 0.9 - 1 bar (compare Figure 6). This operation mode is especially interesting for processes which demand a constant feed temperature. In this case the thermochemical storage reactor can buffer fluctuations of the feed temperature. Beyond that, the temperature of the thermochemical storage system is precisely adjustable by the variation of the vapour pressure.

As a second process application for the thermochemical storage system, the heat generation mode is of interest. In the heat generation mode the storage system is at a low temperature for example after a cooling period due to the unavailability of a heat source. Triggering the exothermal reaction can then lift the entire system to a higher temperature level.

Figure 9 shows the temperature trend for the air inlet and the storage temperatures for the heat generation experiment. In accordance, at the beginning the complete system was in steady state at the low temperature level of 350 °C. At minute 10 the evaporator was connected to the reactor and the pressure in the reactor rises to 0.9 bar. In consequence of the initiated reaction the temperatures T5, T11, T13 raise immediately until they reach the corresponding equilibrium temperature of 490 °C. In the rear area of the reactor this temperature remains for around 150 minutes (compare T13).
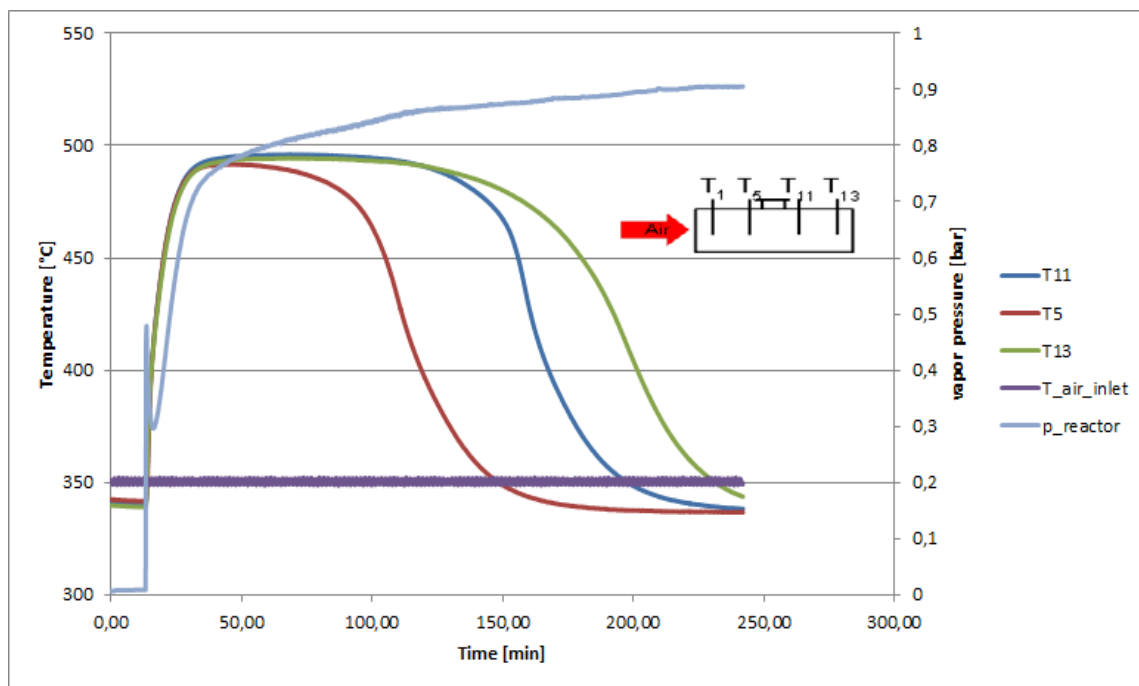

Figure 9 temperature trend during discharge in heat generation mode

Based on this experiment it can be stated that the possibility to lift the storage system to a higher temperature by means of a thermochemical storage was demonstrated. This operation mode might be of special interest for instance in order to support start up processes of various devices.

5. Summary and conclusions

Even though it has been already demonstrated that $Ca(OH)_2$ is a promising reaction system for thermochemical heat storage [1], two crucial question still have to be solved: the development of adapted and efficient reactor concepts as well as integration strategies for the thermochemical heat storage. Both aspects have been addressed in this work.

In order to improve the flowability of fine calcium hydroxide powder the addition of nanoparticles to increase the roughness of the particles has been analysed. The modified material was filled in a gravity-induced reactor under ambient conditions to investigate the movement of the bed. Compared to pure calcium hydroxide a continuous moving bed could be realized with the modified material. Ongoing work in this field focusses on the investigation of the moving bed at elevated temperatures including the chemical reaction.

Simultaneously, different operation modes for the storage material were investigated in a 25 kg pilot reactor. The storage reactor was charged at 450 °C. Discharging was first performed in buffer storage mode. In this mode the inlet temperature dropped from 500 °C to 350 °C while the storage temperature was kept constant due to the ongoing exothermal reaction at 490 °C. Additionally, the heat generation mode – that is only possible with thermochemical storages - was demonstrated where the system was initially cooled down to 350 °C and lifted up to a temperature of 490 °C by the heat of reaction.

In summary, based on the determined operation modes suitable integration concepts for different applications can be derived. A lower charging temperature at about 400 °C as well as higher discharge temperatures would enhance integration possibilities and are currently investigated.

6. Acknowledgements

7. References

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