PHASE CHANGE SLURRIES AS COLD STORAGE FLUID WITH HIGH ENERGY DENSITY FOR SOLAR COOLING

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1. Abstract

This paper presents the application of a high energy density fluid as cold storage medium in a solar cooling system. One possible realization of solar cooling plants is the combination of solar thermal collectors and thermally driven absorption chillers. The system availability depends on insolation and these plants cannot be driven only related to the cold demand. Thermal storages are needed in the system to balance between the required demand of cold and available solar energy to generate cold. Due to the fact, that the temperature difference in cooling systems normally is very small, the energy density of water is quite poor. Phase change slurries (PCS), which are using paraffin as phase change material (PCM) can extend the energy density through the latent heat of the melting/crystallizing of paraffin. For example, in the common temperature range from 6 °C to 12 °C the usable heat capacity of the PCS with paraffin as PCM is about two times higher than that of water. A further extension of the energy density seems possible in the combination of the paraffin/water dispersion and CO2 gas hydrates.

2. Nomenclature

COP	Coefficient of performance
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
O	Oil
PCM	Phase change material
PCS	Phase change slurry
W	Water

3. Introduction

On the one hand solar cooling is a very dynamic application, because of the continuously change of solar insolation and cold demand during operation. On the other hand solar cooling plants based on absorption chillers are slowly reacting to load changes, so that thermal energy storages with high heat capacities are needed to ensure functionally adequate systems. Especially at fast increasing cold demands, which cannot be covered and at fast decreasing cold demands, which can possibly lead to freezing the evaporator of the chiller, operating without a storage is not conceivable. Otherwise the chiller loses efficiency (Zetsche 2008) or even gets damages. But because cold storages only use a quite small temperature interval between 6 °C supply temperature and 12 °C return temperature and a heat capacity of 4.18 kJ/(kg K), the energy density of water storages is so low, that it is sometimes difficult to install an adequate volume, because floor space in machinery rooms is often limited and the costs for vessels increase with its volume.

To enhance the energy density PCM storages, which are using the latent energy of melting / freezing at a certain temperature, are getting attractive. So they are providing a significantly larger energy density. Ice storages for example are already a commercial product for a few years. But their disadvantage is a significant lower coefficient of performance (COP) of the chiller, because of the low temperature to charge the storage. Furthermore, the bigger temperature difference between storage medium and the ambient leads to higher losses to the environment, so proper and consequently costlier insulation is necessary. Another problem is

the considerable lower power output of ice storages. The surface of the heat transfer area in such systems has to be very large and complex as mentioned in Agyenim et al. (2010).

By using PCS, a combination of the advantages of PCM storages (for example ice) and conventional water storages is possible, without having their disadvantages. A PCS storage consists of a liquid fluid like water and therefore has a better heat transfer and higher power than pure PCM. And due to the PCM dispersed in the slurry its heat capacity is much higher than that of water.
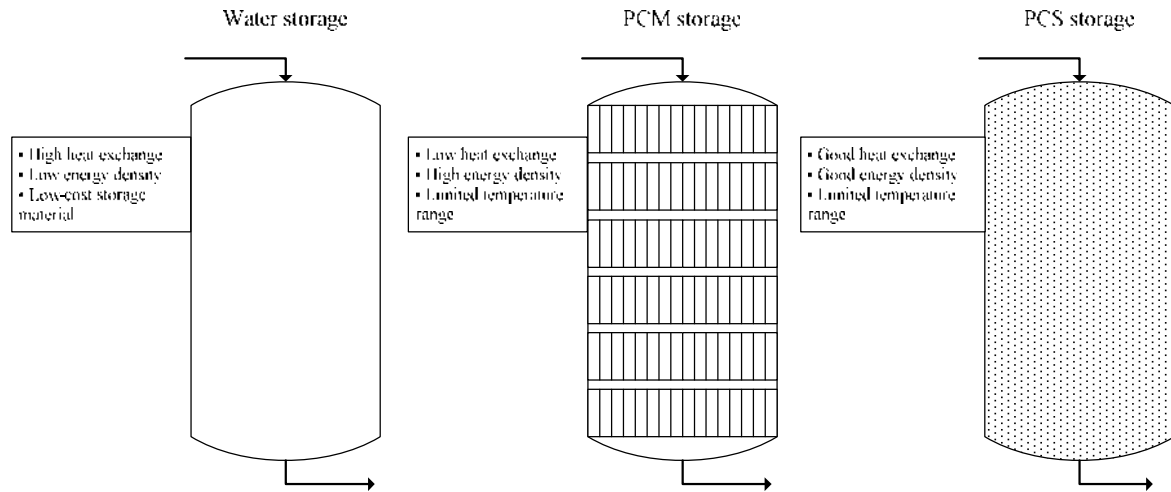

Water storage	PCM storage	PCS storage
• High heat exchange • Low energy density • Low-cost storage material	• Low heat exchange • High energy density • Limited temperature range	• Good heat exchange • Good energy density • Limited temperature range

Figure 1: Characteristics of different storage materials

4. Thermal energy storage:

There are a few systems for thermal energy storage already on the market. So new storage systems should improve as many aspects as possible and fit the requirements of cold storage, which are outlined by Abhat (1983).

Requirements

The energy density has to be high and suit the temperature band of the planned application. To significantly improve a water based storage system, the energy density should be not less than double compared to water. To prevent environmental problems the fluid has to be non-toxic and not or low hazardous to water. Corrosive materials should be avoided too, so existing technology of conventional systems can be used furthermore and do not need special maintenance. Another important aspect is the thermal and chemical stability of the storage material. Also a biological stability has to be ensured in many cases. And the materials have to be available at competitive costs for a long term.

For small and cost-effective storage systems a high power in- and output of the storage material is needed, so heat exchangers can be built as small as possible. Water has the advantage of being pumpable and causing low pressure drop and can be used as storage and cooling fluid. Low viscous PCS share this benefit, so that heat exchangers can be saved.

State of the art

Todays thermal energy cold storage is either a water storage or an ice storage. Both have in common, that the storage materials are cheap and easy to handle. Expressed simplified, a water storage is just a water filled tank with a heat exchanger. Commonly the water is used directly as cooling fluid too, so there is only one heat exchanger needed. But the water storage is strong limited. The energy density is given by the temperature difference, which is normally 6 K at cooling applications, and the heat capacity of 4.18 kJ/(kg K). Therefore ice storages have been developed. They have a higher usable heat capacity, but are more complex. Due to the low heat exchange of melting and freezing ice, a large heat exchanger area is needed. Another disadvantage is the low temperature, which is several degrees below the application and decreases the COP of the chiller. Additionally the thermal losses are bigger and so a better insulation is required. And finally, ice can not be pumped, why another cooling fluid cycle is necessary.

Beside ice storages, other PCM storages are already feasible, but have not asserted on the market yet. The main focus of the development work of the PCM storages is the design of the heat exchange with the objective to enlarge the heat exchange area. An overview is given by Agyenim et al. (2010). Investigated options are macroencapsulated PCMs, PCM-Panels or different kinds of heat exchangers inside the storage tank (Chow et al. 1996), Esen et al. (1998). Typically used PCMs for low temperature applications besides ice are paraffin and stearic acid (Agyenim et al. 2010).

Due to the fact that the heat exchange of PCMs is very low, caused by low thermal conductivity and limited convection, the technical effort to realize the storage is very high. At experiments Butala (2009) needed a storage and equipment of 12.6 kg for a PCM mass of 3.6 kg. The low heat exchange is not only caused by material properties but also due to freezing of the PCM on the heat exchangers (Griffiths 2007, Hawlader et al. 2003).

PCS were developed, which are a combination of water and PCM, to increase the heat exchange and for direct use as cooling fluid. The storage material is dispersed in a liquid and composes a slurry. Possible forms are homogeneous dispersions, like ice slurries, and heterogeneous dispersions like microencapsulated or emulsified PCM. As slurry the storage material can be pumped even when the PCM is in solid state.

A new kind of storage material, gas hydrates, provides promising opportunities for further enhancement of the thermal properties of the storage medium. Their heat capacity is even higher than that of ice and depending on pressure and additives the melting temperature can be varied in a wide range.

5. Objective

The objective of this work is showing the advantages of PCS storages and its application in solar cooling plants. A PCS storage is a combination of conventional water thermal energy storages with a PCM, to enhance the energy density compared to water, but keeping the advantages of a water storage, what means simplicity in design and power in- and output. The new developed PCS storage system does only need a slightly larger heat exchange area for the power input from cooling machines and can be pumped as fluid directly through tubes and systems for cold distribution. Compared to water, the pressure drop is just little higher. So the equipment used for conventional systems can be used without major changes. Even the upgrade of consisting systems is possible, for example to improve an undersized storage for a better utilization of the cooling system.

6. PCS

Microencapsulated paraffin

Microencapsulated paraffins consist of an inner material, the paraffin and an enclosing capsulation material, for example Polymethyl methacrylate (PMMA). At Fraunhofer ISE some investigations with this kind of PCS have been made. Together with water the capsules form a suspension, which has a good heat exchange caused by flowing through heat exchangers. The exchange of thermal energy is inhibited only little by the capsule shells. In the past, possible PCS concentration has not exceeded 30 %, so the energy capacity was not as high as in dispersed systems. Additionally the capsule shells could get damaged by shear forces of the pumps and thermal cycles (Gschwander 2005). In conclusion the work of our group is focused on PCS dispersions.

Dispersion based on paraffin and water

Paraffin/water dispersion is a colloidal system in which fine paraffin droplets are dispersed in water. Due to their immiscibility, paraffin and water tend always to separate. The dispersion was stabilized by a non-ionic emulsifier which is adsorbed at the interface between the paraffin and water and prevents the paraffin droplets coalescence (see Figure 2 left). In this work a high-purity paraffin, Parafol 14-97 of Sasol Company was used. This paraffin has the melting point at 6 °C and the heat of fusion value of 220 kJ/kg and is chemically inert to most materials (Butala 2009). To inhibit the supercooling effect of the dispersions a nucleating agent (paraffin with a higher melting temperature) was used.

To create an emulsion, mechanical energy is supplied to break up the droplets using an emulsifying machine

(rotor – stator disperser PT1300D of Kinematica AG). Figure 2 right shows the external aspect of paraffin/water dispersion.
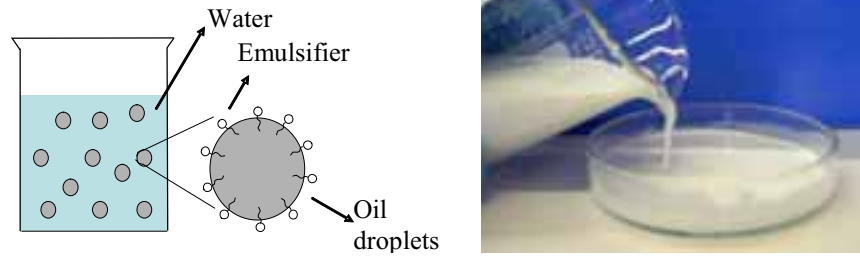

Figure 2: Illustration of paraffin/water dispersion (Huang et al. 2009)

Droplet size and distribution

The droplet size distribution was measured with a Malvern Mastersizer 2000 instrument by laser diffraction technique. Droplet size and droplet size distribution give important information about the paraffin/water dispersion. Dispersions having small droplet sizes present an improved stability compared to big droplets dispersions. In the same time smaller droplet sizes leads to a larger supercooling degree. As can be seen in the Figure 3, the droplet sizes of the dispersions are in the range of 1 to 10 µm.
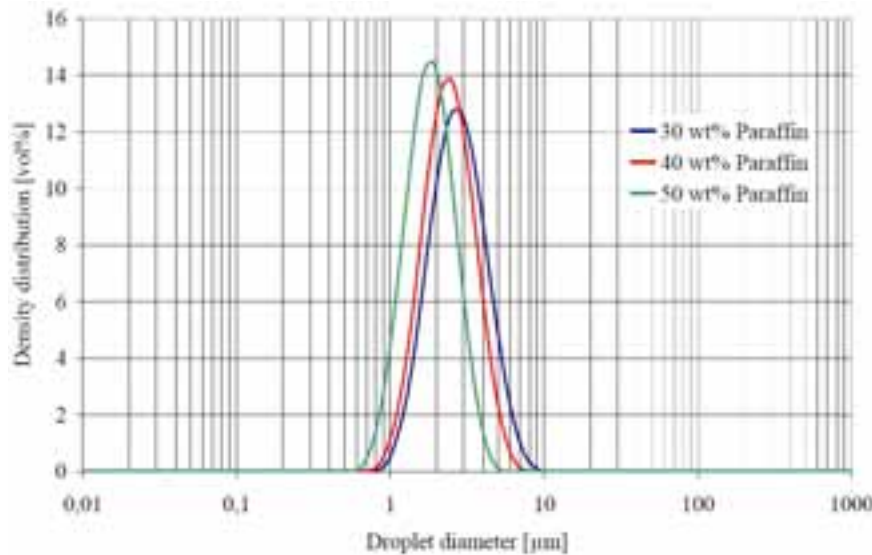

Figure 3: Droplet size distribution of CryoSol^{plus} 6 with different paraffin concentration

Rheological behaviour

The viscosity of paraffin/water dispersion was investigated with a rotation viscosimeter Bohlin Gemini TM of Malvern Instruments Ltd using a cone and plate measurement cell. The cone angle is 4°, the diameter is 40 mm and the gap at the cone tip is 30 µm. A shear stress ramp test was conducted at 10°C for dispersions with different weight fractions of paraffin. As presented in Figure 4 the dispersions viscosity decreases with increasing shear rate and then remains almost constant. The paraffin/water dispersions are pseudoplastic fluids showing a shear-thinning behavior. In the same time an increase of the viscosity by increasing paraffin weight fraction is observed.
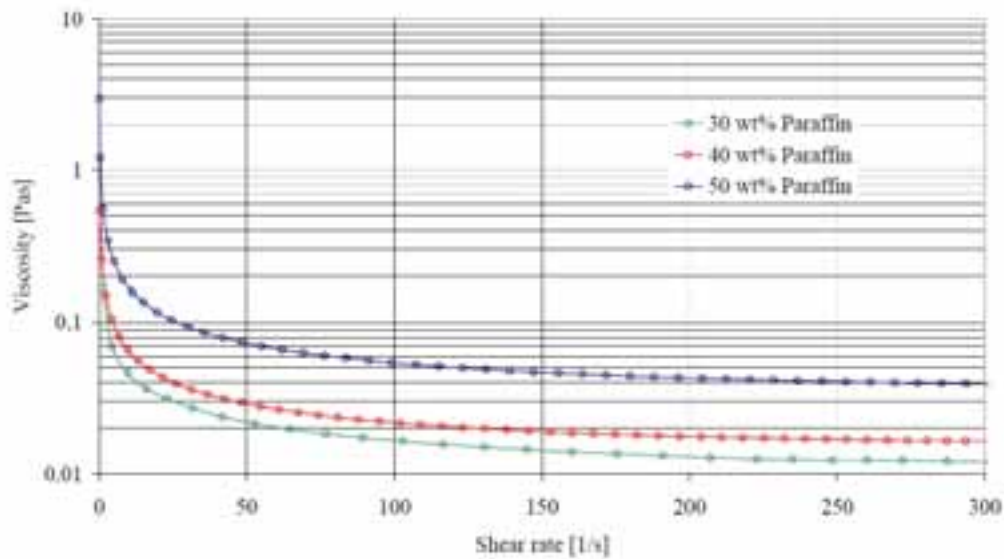
Figure 4: Viscosity of dispersions with different paraffin concentration versus shear rate at 10 °C

Gas hydrates

Hydrate slurry consists of gas hydrate particles dispersed in an aqueous solution. Hydrate slurry production has the advantage of being formed using a non-mechanical process. That avoids the limitation of power input, which is restricting the generation of ice slurries.

Studies on CO_2 hydrates for the service of refrigeration and cold production areas are significantly increasing. That situation is mainly due to the hydrates high enthalpy of dissociation and to its non-mechanical production. Gas hydrates can be directly generated by gas injection into an aqueous solution. The dissociation enthalpy of CO_2 hydrate is around 500 kJ/kg (Marinhas et al. (2006) and Kang et al. (2001)), which is 50 % higher than that of ice (333 kJ/kg).

Gas hydrates are crystalline compounds, similar in look to ice, that are composed of water and gas (or liquid) molecules. They are generally formed under high pressure and low temperature according to equation 1 with n as the hydration number, M as the gas (or liquid) molecule and M(H2O)n as the gas hydrate molecule:

$$nH_2O + M \rightarrow M(H_2O)_n \qquad \qquad \textbf{eq. 1}$$

Water molecules (host molecules) form a lattice structure and the gas molecules (guest molecules) occupy the interstitial vacancies of the lattice. The phenomena of inclusion of the guest molecule and the Van-der-Waals attraction between water and gases stabilize the hydrate molecule. The guest molecules can vibrate and rotate freely within these vacancies or cavities, an assumption which is important to the molecular theory. The gas molecules are too large to move freely through the lattice and each one is localized in a single cavity.
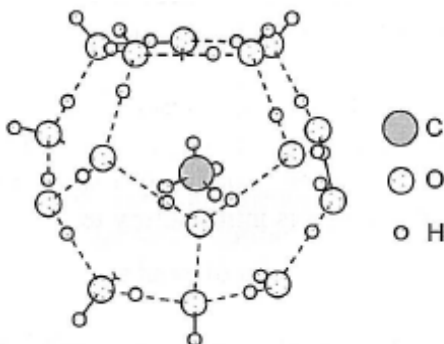

Figure 5: Hydrate structure (Mehling et al. 2008)

Combination of gas hydrates and paraffin-dispersions

Lachance et al. (2008) have studied the impact of gas hydrate formation/dissociation on W/O emulsion stability. The conclusion was that hydrate formation/dissociation phenomena can destabilize emulsions and can lead to a free water phase through agglomeration and coalescence of the dissociated hydrate molecules. In the same time, an increased concentration of emulsifier can prevent the hydrate-emulsion system destabilization.

First experiments were conducted on a sample of CryoSol[plus]20, which was chosen due to its theoretical stability, high fusion enthalpy, phase change temperature and little subcooling degree. (Huang et al 2010)

Phase change enthalpies and temperatures of the emulsion and emulsion-CO_2 system were measured using a DTA experimental device. A full description of this equipment was provided by (Fournaison 2004; Lin 2008). The following experimental procedure was used in order to detect phase changes and to measure their corresponding enthalpies and temperatures.

- Injection of 20 g of the paraffin emulsion into the sample cell at 30 °C (T_1). At that temperature the paraffin remains liquid. A mixture of water (2/3 wt.)-ethanol (1/3 wt.) having the same weight is also injected into the reference cell. The liquids were introduced into each cell by using a glass syringe (brand Ellipse) with a high volume precision (0.1 mL). The syringe is weighted before and after the injection allowing the good knowledge of the injected liquid weight.

- Introducing carbon dioxide directly into the reference cell at the desired pressure at T_1.

- Maintaining the solution at 30 °C till pressure stabilization. In that case, the maximum amount of CO_2 solubility in the emulsion is reached.

- Decreasing the temperature till T_2. T_2 should be at least five degrees lesser than the theoretical crystallization temperature of gas hydrate. The system is maintained at T_2 for few hours.

- The temperature is afterward increased up to 30 °C by using a temperature ramp. This temperature value of 30 °C is significantly higher than the theoretical fusion temperatures of all our paraffin emulsion samples.
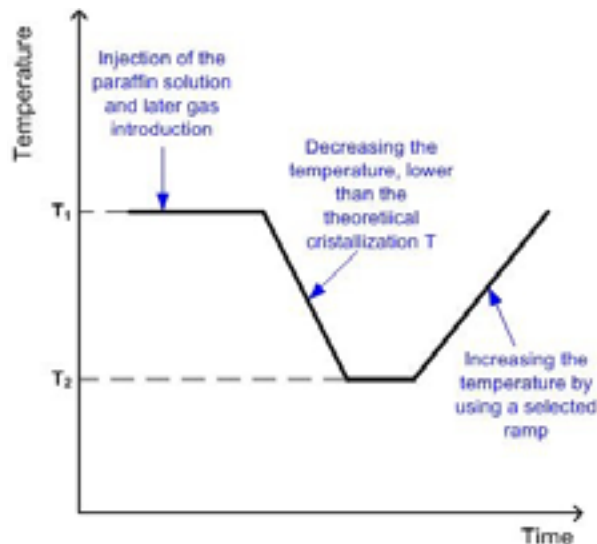
Those steps are resumed in Figure 6.

Figure 6: The used experimental procedure to study paraffin emulsions

The used temperature ramps are 0.01 °C/min for gas hydrate and ice melting, and 0.055 °C/min for paraffin melting. The instrument was previously calibrated with ice. For all measurements, the latent heat enthalpies are determined by integrating the surface area of the fusion peaks, which is multiplied by the ice calibration coefficient.

Heat capacities

Paraffin/water dispersion:

The phase transition temperature intervals and the heat of fusion of the paraffin/water dispersions were measured using a differential scanning calorimeter (DSC) apparatus Netzsch DSC 204. The temperature heating rate was 2 °C/min and the samples mass between 5 and 10 mg. The DSC melting curves of the dispersions containing 30 to 50 wt.-% paraffin are given in the Figure 7. The phase change temperature interval is from 4 to 7 °C and the melting peak point is 6 °C. The peak area of the melting curve corresponds to the heat of fusion of the paraffin/water dispersion.
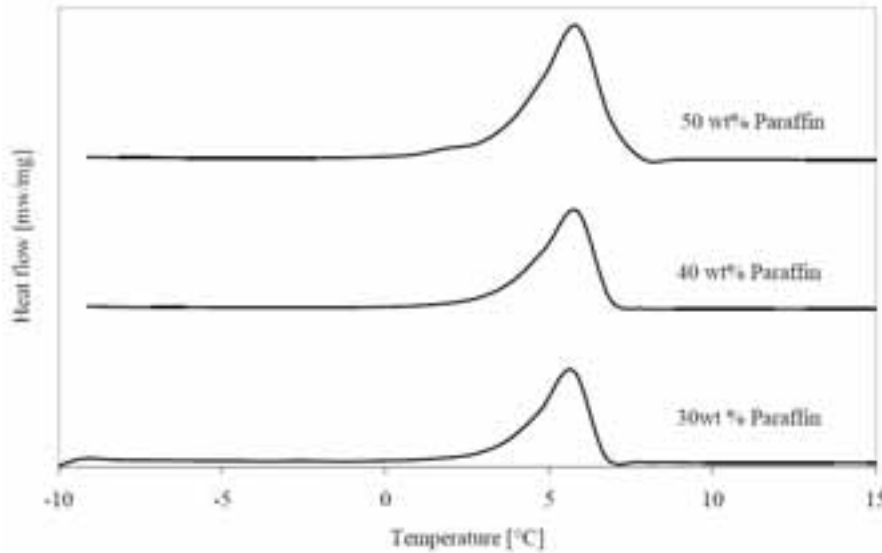

Figure 7: DSC melting curves of the emulsion containing 30 to 50 wt.-% paraffin

The total heat capacity of the dispersion (Δh_d) in a given temperature range consists of the latent heat capacity of paraffin, the sensible heat capacity of water and the sensible heat capacity of paraffin, as shown in equation 2.

$$\Delta h_d = X_p \cdot \Delta h_{f,p}(T) + X_w \cdot c_{p,w} \cdot (T_2 - T_1) + X_p \cdot c_{p,p} \cdot (T_2 - T_1) \qquad \textbf{eq. 2}$$

where X_p and X_w represent the weight fraction of paraffin respectively water, $\Delta h_{f,p}$ is the paraffin heat of fusion in the temperature interval T_1 to T_2, $c_{p,w}$ is the specific heat capacity of water (4.18 kJ/kg K) and $c_{p,p}$ is the specific heat capacity of the paraffin (2.1 kJ/kg K). (Huang et al. 2010)
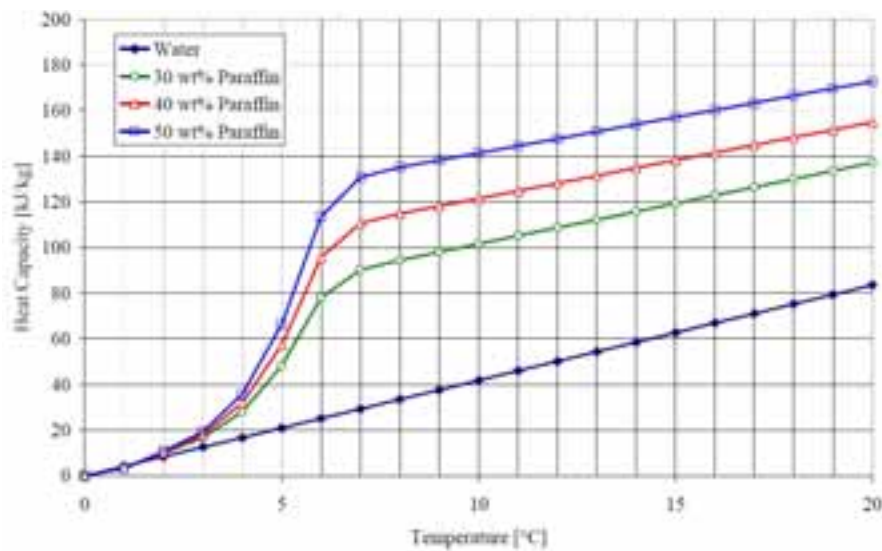

Figure 8: Total heat capacity of dispersions versus temperature compared to water
Figure 8 presents the total heat capacity of dispersions with 30, 40 and 50 wt.-% paraffin compared to water

heat capacity from 0 to 30 °C. In the temperature range 2 to 8 °C the dispersions have a higher energy density than water. For example in the temperature interval 2 to 8 °C the dispersion with 30 wt.-% paraffin has a total heat capacity of 85 kJ/kg which is 3.4 times as high as that of water (25 kJ/kg).

Combination of hydrates and paraffin/water dispersions:

Two different gas injection systems were used.

The first consists of continuously injecting the gas into the experimental system. Such system, called continuous injection system, allows a good stabilization of the pressure independently of the temperature, but it limits the detection of gas hydrate by pressure drop.

The second system, called closed injection system, consists of closing the system once the maximum amount of CO_2 solubility is reached. Such system allows a good detection of gas hydrate by pressure drop, but the pressure is decreased when the temperature is decreased.

First experiments done under CO_2 pressure are represented in Figure 9. In the first one, the CO_2 pressure is 3.7 bar and in the second it is 25 bar. They occur respectively in a closed and continuous injection system.
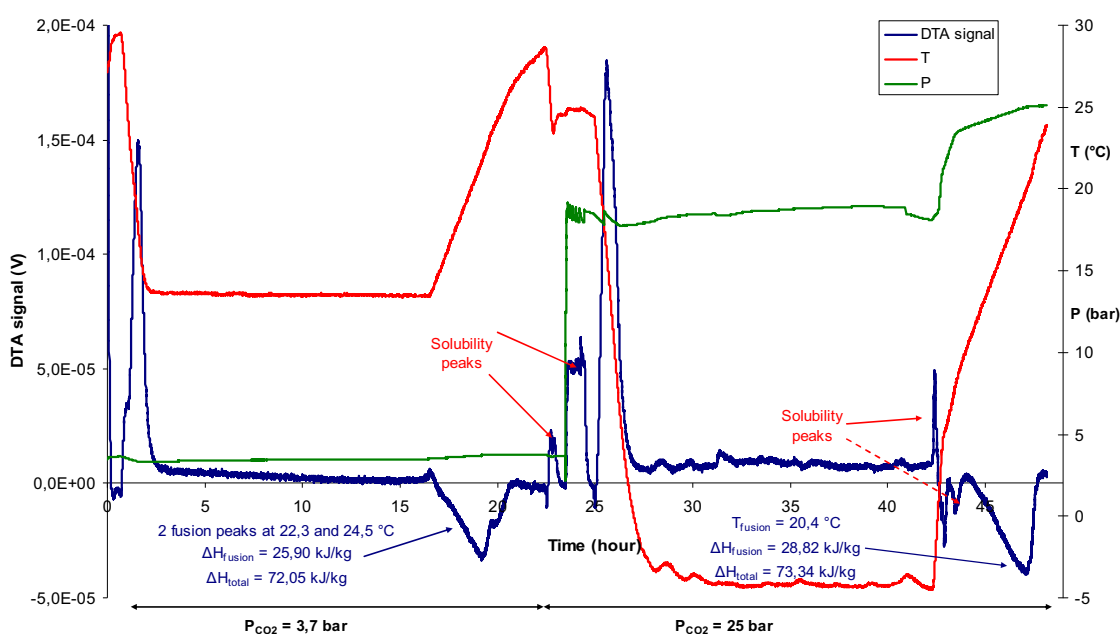
Figure 9: The behaviour of the emulsion solution under 3.7 and 25 bar of CO_2

The first experiment was performed at 3.7 bar and two fusion peaks at 22.2 and 24.5 °C were detected. The latent heat of fusion and the total heat of the emulsion are respectively 25.9 and 72.1 kJ/kg. As for the second experiment, achieved under 25 bar, there is only one single fusion peak at 20.4 °C. The latent heat of fusion and the total heat of the emulsion are respectively 28.8 and 73.3 kJ/kg.

In Figure 10 can be observed that the CO_2 solubility in the emulsion is relatively high. The corresponding solubility peaks can't be neglected. In general, the solubility enthalpy of CO_2 in water represents around 10 % of the dissociation enthalpy of CO_2 hydrate. This proportion seems to be higher in the case of paraffin-water emulsion. Theoretically, under the used experimental conditions, CO_2 hydrate had to form at 7.8 °C but its formation attempt failed even at -4 °C. It is assumed that the models that predict gas hydrate formation has a difficulty to predict it in the presence of hydrocarbon phase. In fact, those models were based on the triphasic equilibrium liquid water – gas hydrate – vapour. Thus, it is expected that CO_2 hydrate will be formed under tougher conditions: the dissociation pressure should be higher and/or the dissociation temperature should be lesser. The presence of the surfactant even at low concentration might have inhibited CO_2 hydrate formation. This can also be the reason for the failed attempt to form CO_2 hydrate.

Another experiment was accomplished under 19 bar CO_2. In this experiment, the temperature was decreased

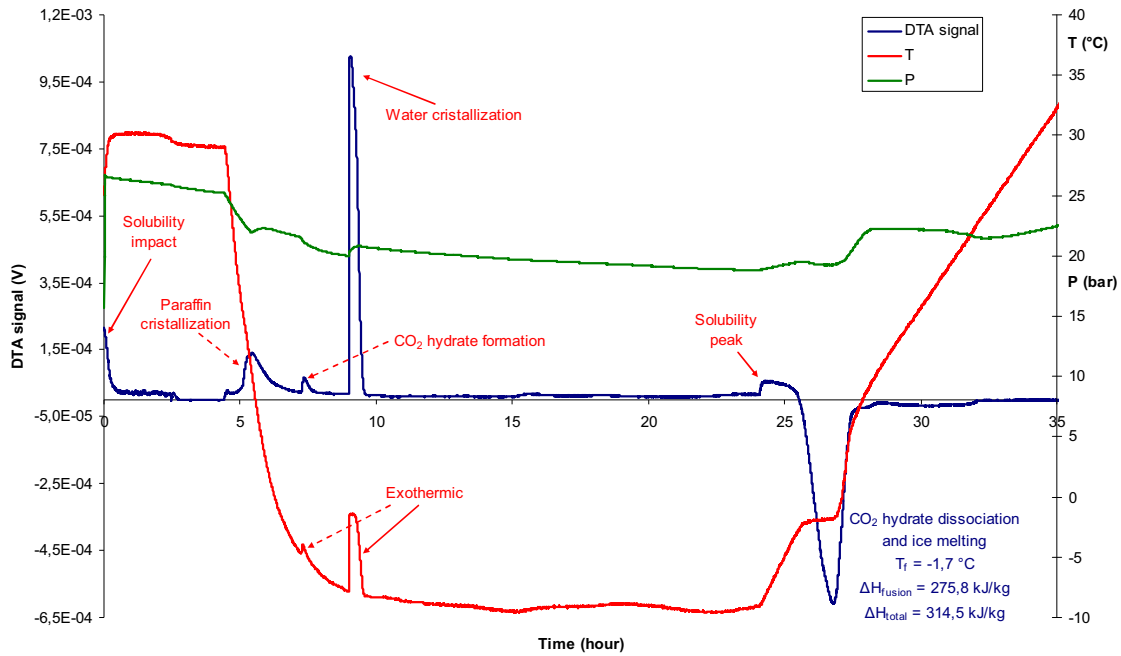till -10 °C in order to favorite CO_2 hydrate formation (Figure 10).

Figure 10: The behaviour of the emulsion solution under more than 19 bar of CO_2

Figure 10 shows the CO_2 solubility impact on the emulsion. At the beginning, the temperature was directly decreased from around 28 °C to -9.5 °C. Three different crystallization peaks were obtained: Paraffin crystallization at around 9 °C, CO_2 hydrate formation at -4.4 °C (theoretical formation at 5.9 °C) and ice formation at -8 °C. CO_2 hydrate formation was accompanied by a small pressure drop, and ice formation was accompanied by a little increase of the pressure, because it is a pure compound. In fact, during the liquid water – solid water transition, the soluble CO_2 in liquid water abandons the liquid phase and hence causes a little pressure increase. The two exothermic peaks are due to ice and CO_2 hydrate formation.

At -9.5 °C, the temperature was stabilized for 15 hours, and then the temperature was decreased in order to melt the solid compounds. Ice and CO_2 hydrate melt at -1.7 °C at the corresponding pressure of 19.3 bar. However, no paraffin melting was detected. The latent enthalpy is 275.8 kJ/kg and the total enthalpy of emulsion is 314.5 kJ/kg.

This experiment shows that CO_2 hydrate can be formed in our system. Gas hydrate was formed under tougher conditions than in the classical binary system of liquid vapour – carbon dioxide vapour. This is probably due to the presence of paraffin and surfactant. The corresponding total enthalpy of fusion is high.

Heat transfers

The enhanced heat transfer is, together with the possibility of being pumped, the major advantage of PCS over PCM. While according to Grigull et al. (1990) water has a heat transfer between 0,561 W/(m K) (0 °C) and 0,679 W/(m K) (99,63 °C) and 0,598 W/(m K) at 20 °C, raw paraffin has only 0,2 W/(m K). It is expected, that heat transfers of PCS are significantly higher than that of PCM, caused by their water basis. Besides, PCS are liquid all the time, so convection effects occur. And when pumped through heat exchangers, turbulent flow also promotes the heat exchange. Experiments for confirmation are in progress at the moment.

7. First design drafts of possible storage systems

At the moment four possibilities to integrate a cold storage based on paraffin/water dispersion into a system are discussed. These four possibilities are depicted in Figure 11.
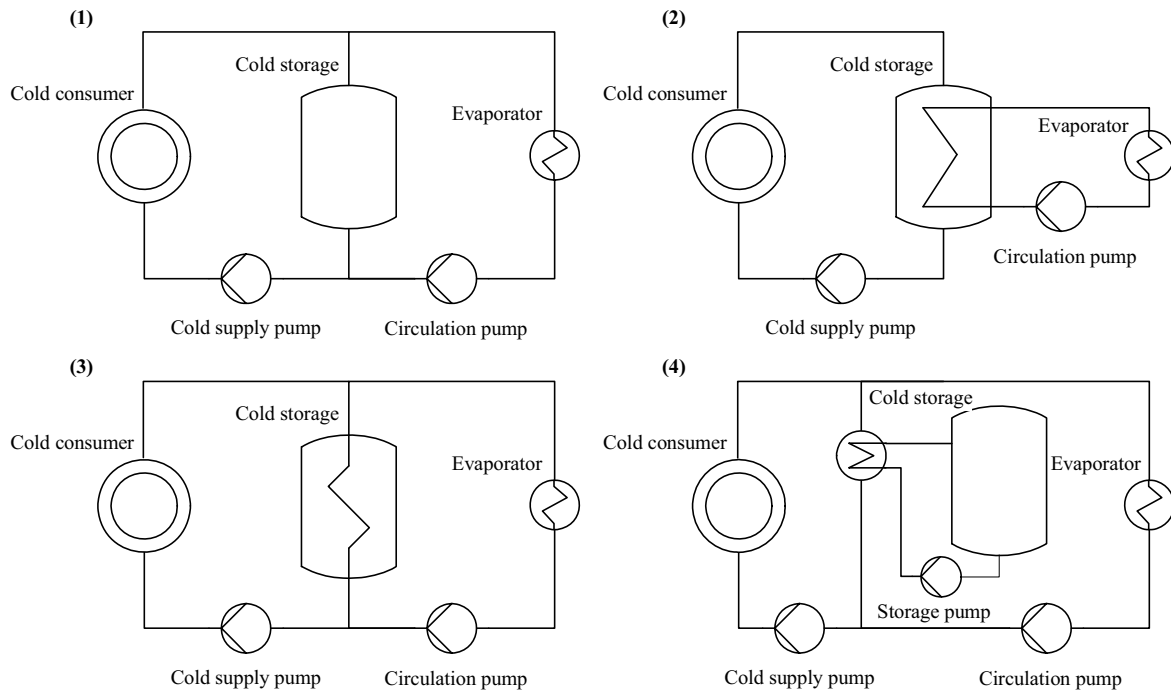
Figure 11: Possible integration of a cold storage based on paraffin/water dispersion into the cooling system

Possibility (1) uses the paraffin/water dispersion directly as cold supply and storage fluid. The paraffin/water dispersion circulates over the evaporator of the chiller, as well it is pumped to the cold consumer. A vessel serves as buffer and cold storage. Higher pressure drops in the cold supply network should be considered and will limit the concentration of the paraffin/water dispersion used. But on account of the higher energy density a lower volume flow is needed and the energy demands for cold distribution decreases compared to water systems. Possibility (2) uses also the paraffin/water dispersion as cold transfer and storage fluid, but there is a hydraulic separation of the chiller loop (evaporator) to the cold storage by an internal heat exchanger in the storage. This hydraulic separation could be necessary if it is not possible to pass with the paraffin/water dispersion through the chiller or only a cold supply sub-system in a cold supply network should operate with paraffin/water dispersion. Possibility (3) uses the paraffin/water dispersion only as storage medium in the cold storage. Also in this case, a hydraulic separation is realized by an internal heat exchanger in the cold storage. The heat transfer between the cold supply fluid and storage medium occurs by heat conductivity and convection, even in the storage, because the storage medium remains liquid. Due to the fact that the paraffin/water dispersion is not pumped, pressure drops have not to be considered and higher paraffin concentration of paraffin/water dispersion could be chosen compared to the possibilities (1) and (2). If the required power of the cold storage can not be achieved because the heat transfer by free convection and conductivity at the internal heat exchanger is not sufficient, an external heat exchanger with a storage pump could be used to obtain heat transfer by forced convection. This is possibility (4).

In view of using hydrates as PCS in a cold supply system, the system must be operated under pressure. The CO_2 has to be injected at the point where the cold supply fluid is charged and the hydrates are formed. It evaporates at the point where the cold supply fluid is discharged and the hydrates melt. The reuse of the CO_2 requires the separation of CO_2 from the cold supply fluid and the return of the CO_2 to the injection point by a compressor. Also the use of hydrates in a cold storage as pure storage medium is conceivable. In that case, CO_2 is injected under pressure at the bottom of the storage into water during the charging process and hydrates are formed. When discharging the cold storage, the pressure is reduced, the hydrates melt and the evaporated CO_2 is withdrawn from the top of the storage. A hydraulic separation between the PCS in the storage and the cold supply fluid, which charge and discharge such a cold storage, prevent the carry-over of CO_2 into the whole cold supply system.

8. Conclusion

Due to the fact that solar insolation and cold demand is not constant over the day, cold supply systems based on solar cooling have to shift energy by thermal energy storages. Furthermore, the absorption chillers, which are often used in solar cooling plants, have a long response time in view of the steadily changing operational conditions of such a system. There are two main possibilities to store thermal energy in the system: on the hot and on the cold water side. Especially the cold water side has the disadvantage that the heat capacity of a cold storage and supply system is very limited due to the small possible temperature difference, so that storage systems using latent heat are in the focus of interest.

Besides ice storage systems, PCS based on oil in water dispersions or hydrates are currently investigated to enhance the heat capacity of cold storage systems. As depicted in the experiment results, paraffin/water dispersions have a heat capacity, which is significantly higher, than that of water. Furthermore the experiments combining the dispersion with gas hydrate slurries, seems very promising. While the dispersion can be used in conventional cooling systems, gas hydrates or gas hydrate-dispersion combinations can only be operated under pressure. For storage systems based on paraffin/water dispersions several concepts are possible. In these the PCS can be used either as storage medium only with a hydraulic separation of the supply network or also as cold carrier fluid in the supply network without hydraulic separation.

At Fraunhofer UMSICHT the application of a PCS storage in combination with a solar driven absorption chiller is planned. It is foreseen to demonstrate the feasibility of such storages as well as to improve efficiency of the solar cooling plant by the cold storage.

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