

# ADSORPTION COOLING SYSTEM FOR COLD STORAGE USING METHANOL/SILICAGEL

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## ABSTRACT

For the cold storage of agricultural products at temperatures of 2-4°C in India a solar-hybrid cooling system is developed, using solar energy from flat plate collectors and the waste heat of a genset, operated with producer gas. A commercially available low temperature (80-90°C) adsorption cooling system for air-conditioning application has to be modified for the operation at cooling temperatures below the freezing point of water. Methanol instead of water is investigated as refrigerant. Because of the inferior thermodynamic properties of methanol and the lower operation temperature, the efficiency will be reduced. Calculations show, that the COP for a commercial adsorption cooling system will be about 30% when operating the system with methanol/silicagel at a chilled water temperature of  $T_0 = -2^\circ\text{C}$ , a heating water temperature of  $T_h = 85^\circ\text{C}$  and a condenser temperature of  $T_c = 30^\circ\text{C}$ . A laboratory test facility with heating and cooling capacities of about 2kW is set up. By comparative experiments with water and methanol the calculations could be validated, though the specific power density is only 1/10 of the commercial system.

**Keywords:** adsorption cooling, silicagel/water, silicagel/methanol, thermodynamic analysis, coefficient of performance, system design, experiments

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## INTRODUCTION

In a tropical country like India the importance of refrigeration can hardly be over-emphasized. Agricultural products play a significant role and could yield substantial foreign trade for the country. However, between production and real sales about 30% of the production is spoiled during storage and transit. This alarming high spoilage rate calls for a greater attention to achieve efficient methods of storage. The most important method used for preventing spoilage is preservation in cold storage. In most Indian cold storages temperatures ranging between  $-1^{\circ}\text{C}$  and  $10^{\circ}\text{C}$  are required. Besides that there is also a smaller demand for freezing at temperatures of  $-18^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ .

Indian food production centers are usually situated in areas where the electrical power supply for the operation of conventional refrigeration plants is either not available or not reliable. Refrigeration plants driven by renewable energy sources represent an attractive alternative [1]. For this application in a project, supported by the European Commission, a hybrid system is developed, using solar energy from flat plate collectors and the waste heat of a genset, operated with producer gas [2],[3].

Due to the use of solar collectors and genset waste heat, the concept requires a refrigeration system which can be driven by heat of a low temperature level. Single stage absorption cooling systems are operated with a fixed temperature difference between driving water inlet and outlet of 5-10 K. High inlet temperatures therefore result in high outlet temperatures, which cause unfavorable

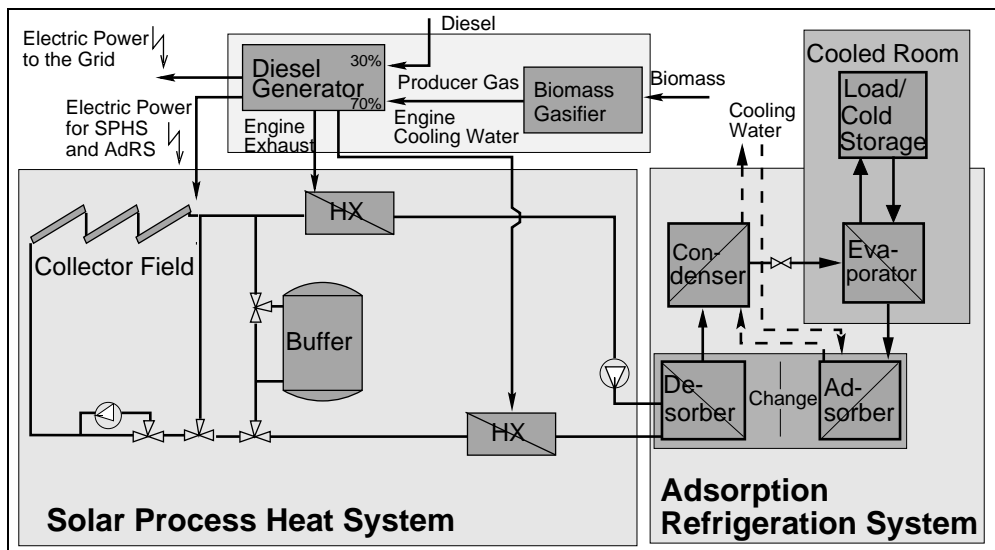


Fig. 1: Draft system design for solar-hybrid adsorption cold storage

operation conditions for the solar field and the genset cooling water heat exchanger. By means of an adsorption system, like the cooling system with the working pair water/silicagel, which is available on the market[4], it is possible to reach cold water temperatures of  $3^{\circ}\text{C}$  with driving temperatures of  $T_h = 85^{\circ}\text{C}$  ( $\text{COP}=0.5$ ,  $T_c = 29^{\circ}\text{C}$ ). This system can already be operated at a driving heat temperature of about  $60^{\circ}\text{C}$ . Thus it would be possible to run the cooling system with flat plate collectors, which might improve the economy because of lower investment costs. In Fig. 1 the draft system design for a solar-hybrid operated cold store is displayed.

Due to the presently used refrigerant water the adsorption chiller is restricted to cooling temperatures above the freezing point of water at  $0^{\circ}\text{C}$ . It will be shown, that by changing to the working pair methanol/silicagel it might be possible to reach cold brine temperatures of  $-5^{\circ}\text{C}$  with an  $\text{COP}=0.25$ .

After an introduction to the thermodynamics a theoretical analysis is carried out for a prediction of the achievable COP using methanol/silicagel. This is validated by experiments with a test facility. To get predictions for the use of methanol instead of water in a commercial adsorption chiller, the data are compared with the operation with water.

## THERMODYNAMICS

### Principle of Operation

The principle of an adsorption cooling system is depicted in Fig. 2. The system is built up with a condenser, a throttle valve, an evaporator and the sorption chamber as thermal compressor.

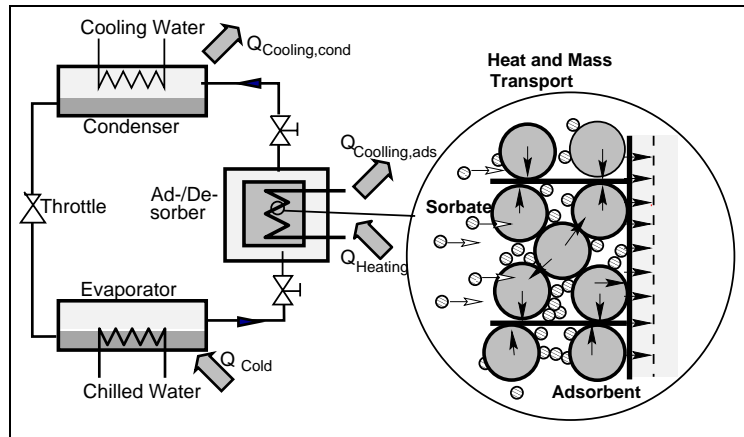


Fig. 2: Working principle of the adsorption cooling system

The thermal compressor is operated in two phases. During the first phase of the operation cycle the refrigerant is evaporated at low pressure and low temperature in the evaporator and is adsorbed by the silicagel in the reaction chamber under isobaric conditions.

In the reaction chamber (ad- and desorber) the refrigerant is adsorbed in the pores of the adsorbent silicagel. The heat of adsorption, which is set free is removed by a heat exchanger in the reaction chamber with the cooling water. The lower the cooling water temperature is the higher the final uptake of refrigerant by the silicagel will be.

After saturation of the silicagel the adsorbent is regenerated by an isosteric heating of the adsorbent and a following isobaric desorption. By this two step ad- and desorption process the refrigerant is compressed. The final pressure for this second part of the cycle is given by the point of saturation in the condenser, which is fixed by the cooling water temperature. Before the next adsorption, the sorbent is cooled down isosteric and the condensed refrigerant is fed by an expansion valve to the evaporator.

The relation between pressure and temperature at steady state conditions is described by the equation of Clausius-Clapeyron

$$\ln \frac{p}{p_0} = -\frac{\Delta h_d}{R} \frac{1}{T} + const.. \quad (1)$$

According to equation [1] the adsorption process can be displayed very well in a  $\log p / -1/T$ —diagram, the Clapeyron diagram (Fig. 3). In this diagram the process is plotted as a trapezium between the isosteres  $C_2$  and  $C_1$  ( $C_1 < C_2 < C_{max}$ ) and the isobares  $p_c$  and  $p_0$ .

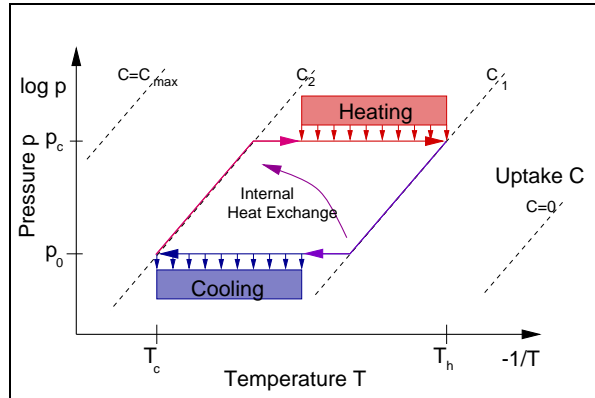


Fig. 3: Clapeyron diagram of adsorption cooling system

The uptake of the sorbent  $C$  varies with the time. Starting from the initial uptake  $C_0$  for infinite times the steady state uptake  $C_{max} = C(p, T)$  is

Refrigerant	$\Delta h_V$ at $p=0.1$ bar in J/g	$\Delta h_D$ at $C=8\%$ in J/g
Water	2400	3020
Methanol	1200	1680

Table 1: Heat of vaporization and adsorption by silicagel [7]

reached, which is defined by the cooling water temperature  $T_c$  and the evaporator pressure  $p_0$ . For isothermal adsorption this process is described according to Sakoda[5] by the differential equation

$$\frac{dC(t)}{dt} = k_s a_p (C_{max}(T_c, p_0) - C_0(T_h, p_c)), k_s a_p = \frac{c_1}{r_{particle}^2} \exp\left(-\frac{c_2}{T}\right) \quad (2)$$

with the temperature depending mass transfer coefficient  $k_s a_p(T)$ .

The cooling power  $\dot{Q}_c$  is proportional to the rate of refrigerant adsorbed. Thus the actual cooling power is given by

$$\dot{Q}_c = \frac{dC(t)}{dt} m_{dryads} \Delta h_{ads}. \quad (3)$$

To reach an equable power output, the system can be modified as two chamber system, which is operated alternating. By an internal heat exchange between the two chambers during the isosteric heating and cooling of the sorbent, the efficiency of the system can be improved.

### Predicted COP for Using Methanol/Silicagel

The coefficient of performance  $COP$  for sorption cooling systems is defined by the ratio of evaporation energy  $Q_0$  to desorption energy  $Q_{des}$ . A thermodynamical analysis gives the limits for the technical possible  $COP$  when operating the adsorption chiller with methanol at  $-2^\circ\text{C}$ .

The  $COP$  of a liquid sorption system is limited by the efficiency given by the two Carnot cycles between the temperatures  $T_c/T_0$  and  $T_c/T_h$

$$COP_{carnot} = \frac{Q_0}{Q_{des}} = \frac{Q_0}{Q_h} = \frac{T_0}{T_c - T_0} \frac{T_h - T_c}{T_h}, \quad (4)$$

with the temperature of the heating source  $T_h$ , the brine/cold water temperature  $T_0$  and the cooling water temperature  $T_c$ . The achievable  $COP$  depends on the operating temperatures according to equation [4]. For lower brine temperatures the maximal  $COP$  decreases due to thermodynamics.

The  $COP_{carnot}$  (equation [4]) is calculated under the assumption that the heat transfers occur at fixed temperature. For a heat transfer at varying temperature, as for a sorption system, based on the definition of the entropy  $\Delta S$

$$\Delta S = \int \frac{dQ}{T} \quad (5)$$

an entropic average temperatures  $T_s$  can be calculated

$$T_{s,i} = \frac{Q_i}{\Delta S_i} = \frac{Q_i}{\int dQ_i/T_i} \quad (6)$$

(with  $i = 0, c, h$ ). The resulting  $COP_E$  will be lower than the  $COP_{Carnot}$  at fixed temperatures

$$COP_E = \frac{T_{s,0}}{T_{s,c} - T_{s,0}} \frac{T_{s,h} - T_{s,c}}{T_{s,h}}. \quad (7)$$

The lower COP of an adsorption system compared to an absorption system can be explained by an entropic analysis of the system, which is shown by Meunier [6]. Due to temperature shifts during the ad- and desorption processes, the maximal COP of the resulting three two-temperature Carnot cycles is limited compared to the COP according to the two Carnot cycles of liquid absorption systems.

The real COP of an adsorption cooling system is influenced moreover by two major subjects (i) the system design and (ii) the physical properties of the working pair. Due to the periodic operation mode of the adsorption process the sorption chamber has to be heated and cooled cyclicly. This results in an additional energy for heating up  $Q_{heatup}$ , which mainly is influenced by the system design. By influencing the phase change energy  $Q_D$  of the refrigerant, the amount of transformed energy during a cycle of operation is affected.

$$COP_{period} = COP_E \frac{1}{1 + Q_{heatup}/Q_D}. \quad (8)$$

Due to a lower specific phase change energy  $Q_D$  of methanol the working pair methanol/silicagel has a lower COP compared to water/silicagel.

Taking into account the losses of the cooling system, it is possible to predict the COP for the methanol/silicagel cooling system (Fig. 4). Based on the given COP of a commercial adsorption chiller, operated with the refrigerant water at  $T_0 = 10/5^\circ\text{C}$  (cold water inlet/outlet temperature) the COP for the operation with methanol at  $T_0 = 3/ -2^\circ\text{C}$  can be predicted. The influence on the COP can be divided in the effect according to the Carnot cycle by changing the working temperature (resulting in an theoretical curve for water at  $T_0 = 3/ -2^\circ\text{C}$ ) and the effect by changing to methanol.

For the evaluation of the influence of changing the working temperature the technical COP is multiplied with the relation of the Carnot-COP at the new working conditions and the starting conditions.

$$COP_{3/-2} = COP_{10/5} \frac{COP_{Carnot3/-2}}{COP_{Carnot10/5}} \quad (9)$$

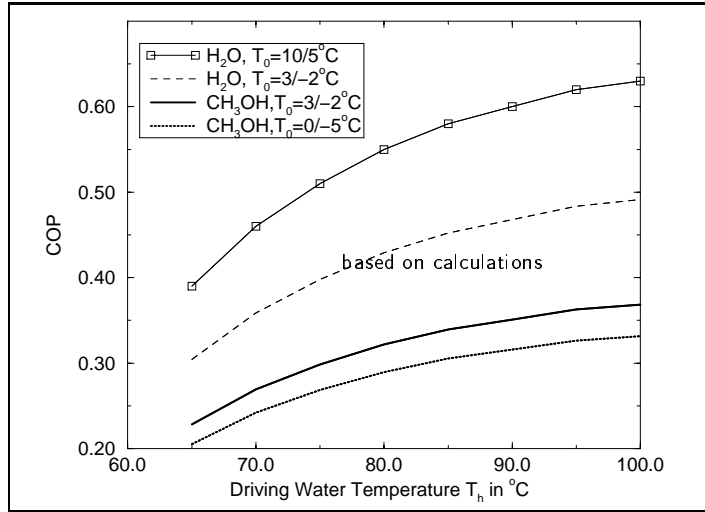


Fig. 4: Predicted COP for using methanol/silicagel

A lowering of the brine temperature thus results in a  $COP_{3/-2}$  for a brine temperature of  $T_0 = 3/ - 2^\circ C$ , which is about 75% of the  $COP_{10/5}$  for  $T_0 = 10/5^\circ C$ .

From equation [8] the influence of the phase change energy of the refrigerant can be deducted. By calculating the ratio of  $COP_{period}$  for using water instead of methanol the effect by this change is determined. The lower ratio of phase change energy to energy needed for heating reduces the COP for methanol/silicagel additionally of about 25% compared to the system water/silicagel ( $COP_{CH_3OH} \approx 0.75 COP_{H_2O}$ ).

Thus the predicted COP for methanol at the brine temperature of  $T_0 = -2^\circ C$  is about half of the COP for water at the cold water temperature of  $T_0 = 5^\circ C$ . Based on the data of a commercial water/silicagel chiller the COP for the methanol/silicagel system will range between 25-32%, depending on the driving water temperature.

## EXPERIMENTS

### Laboratory Test Facility

A laboratory test facility has been built up (Fig. 5), to examine the real operation conditions for an adsorption cooling system with the working pair methanol/silicagel.

The maximum capacity of the components of the test facility is about 2 kW, depending on the working pair and the operating temperatures (Tab. 2). In the

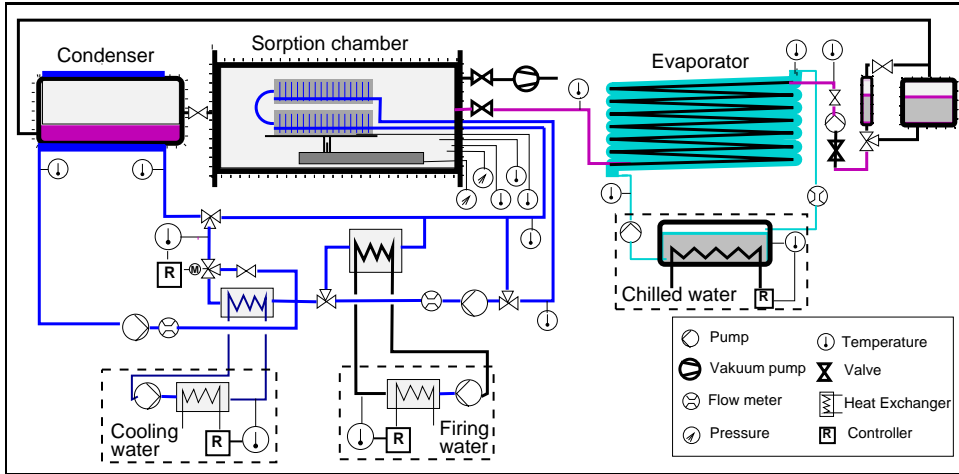


Fig. 5: Scheme of the adsorption test facility

Sorption chamber	Volume	23.9 l
	Mass of silicagel	0.6 kg
Cooling water	Temperature range	0-40 °C
	Power at (20 °C)	2 kW
Firing water	Temperature range	20-95 °C
	Power	6 kW
Evaporator	Temperature range	-5 - +30 °C
	Power (at 0 °C)	2 kW

Table 2: Data of the adsorption test facility

sorption chamber a finned tube heat exchanger packed with silicagel is placed on an electronic compensating scale to record directly the weight of the sorbent. Thus the uptake of the silicagel with refrigerant can be evaluated. Additionally pressure and temperature in the reaction chamber are recorded. For all heating and cooling loops mass flows as well as inlet and outlet temperatures for the heat exchanger are measured by inductive flow meters and platinum resistance thermometers, to calculate the heat transferred within the components. A tubular shell is used as condenser, which is flanged to the sorption chamber by a slide valve. The outer shell is tempered by the cooling water of a thermostate. The condensate is pumped to a coaxial pipe evaporator for evaporation. The evaporator is connected with the sorption chamber by a ball valve.

Instead of a two-chamber system as installed in the commercial unit for the test facility, only one adsorption chamber is used. Due to the down scaling also the dead mass ratio of the test facility (the ratio of the mass of the active sorbent to the mass of the heat exchanger) is worse. Because of these modifications the test facility differs in its results. In addition it was observed that the sorption



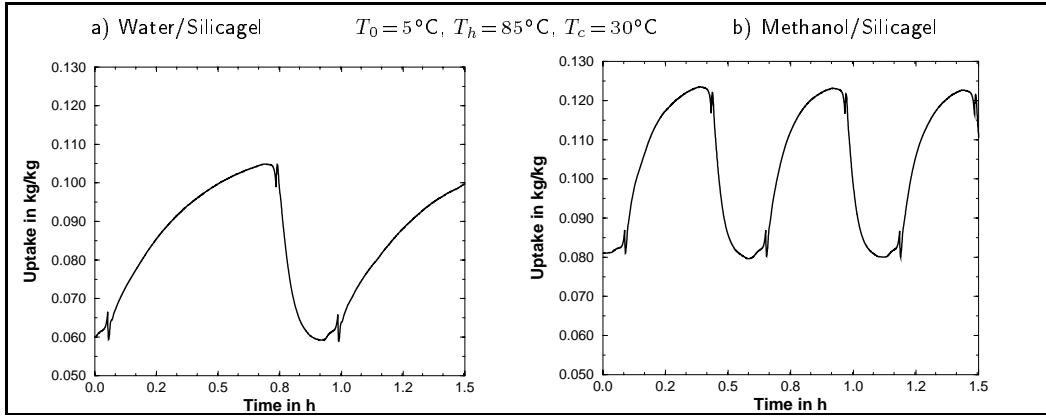


Fig. 6: Measured uptake for a) water/silicagel and b) methanol/silicagel

kinetic for the silicagel used in the test facility is much slower compared with the results for the silicagel of the commercial system.

To study the effect of the different physical properties (e.g. the boiling temperature), experiments with water and silicagel are carried out. With these results predictions for a modified chiller can be achieved by up-scaling.

### Refrigerant Water

Consecutive cycles of ad- and desorption are carried out at operation conditions of heating water with  $T_h = 85^\circ\text{C}$ , cooling water  $T_c = 30^\circ\text{C}$  and an evaporator temperature, which corresponds to the chilled water temperature of  $T_0 = 5^\circ\text{C}$ . Between ad- and desorption phase the sorption chamber heat exchanger is operated for some minutes in bypass mode. Thus the heating/cooling loop is tempered for the new operation temperature. This also corresponds to the internal heat exchange phase of the two-chamber system.

In Fig. 6a 1.5 cycles are displayed. Each of the adsorption phases takes about 50 min, whereas the desorption is completed in about 15 min. The time difference is mainly caused by the temperature dependence of the mass transfer coefficient  $k_s a_p$  (equation [2]). Including the bypass operation a complete cycle takes about 70 min. The uptake of the silicagel oscillates at the given conditions between 6 and 11%. This corresponds quite well with the data from isosteric charts of Khelifa for the silicagel ‘Troockenperlen N’[7]. Deviations in the maximum and minimum values are caused by variation in the heating or cooling temperatures.

During the adsorption the pressure in the chamber is set by the adsorption process with regard to the evaporation pressure of water in the evaporator  $p_0(T_0 = 5^\circ\text{C}) = 10 \text{ hPa}$ , which gives the upper limit. For a cooling water

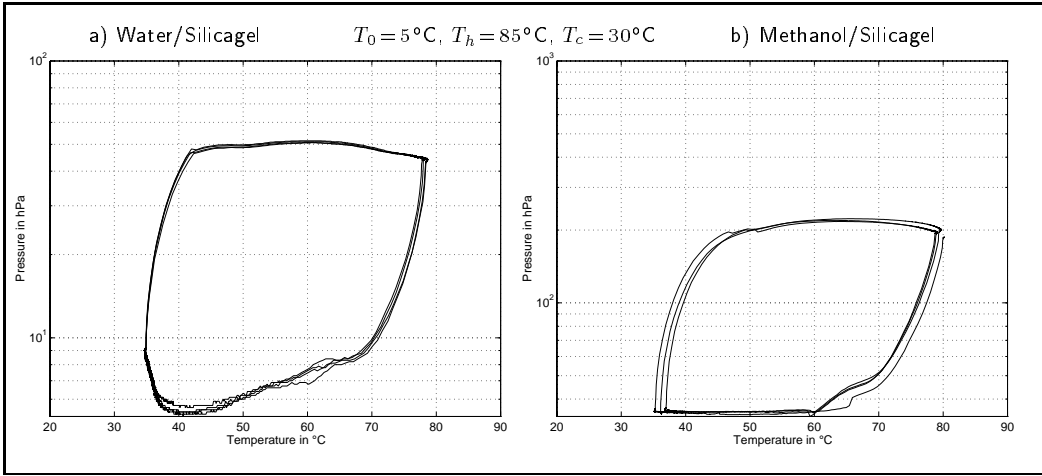


Fig. 7: Measured temperature-pressure curve in the Clapeyron diagram for a) water/silicagel and b) methanol/silicagel

temperature  $T_c = 30^\circ\text{C}$  the resulting maximum uptake  $C_{max}$  is 15%. If this temperature is not reached in the sorbent the maximum uptake will be reduced (e.g.  $C_{max} = 11\%$  for  $T_c = 35^\circ\text{C}$ ). The maximum value is reached after an infinite period of time whereas at technical applications the process is stopped earlier, to improve the power density. The minimum uptake is limited by the heat source temperature  $T_h = 85^\circ\text{C}$ . With the condenser pressure  $p_c(T_c = 30^\circ\text{C}) = 40$  hPa the ideal limit is close to 4%. Due to the limitations of the technical process and the temperature gradient in the silicagel only an oscillation between 6 and 11% is reached in the experiment for  $T_c = 30^\circ\text{C}$ ,  $T_0 = 5^\circ\text{C}$  and  $T_h = 85^\circ\text{C}$ .

Plotting the pressure in the sorption chamber as a function of the temperature of the sorption chamber (Fig. 7a), the result corresponds to the ideal cycle displayed in Fig. 3. The pressure level for isobaric ad- and desorption is fixed by the evaporator and the condenser temperature, whereas the isosteric heating and cooling is fixed by the temperature in the heat exchanger of the sorption chamber.

### Refrigerant Methanol

Operating the system at the same border condition as for water, the resulting loading is nearly the same when using methanol as refrigerant (Fig. 6b). The uptake during adsorption at an evaporator temperature of  $T_0 = 5^\circ\text{C}$  ( $p_0 = 28$  hPa) and a cooling temperature of  $T_c = 30^\circ\text{C}$  is nearly 13.5%. The regeneration of the adsorbent reaches 8.5% at a heating water temperature of  $T_h = 85^\circ\text{C}$  and a condenser temperature of  $T_c = 30^\circ\text{C}$ .

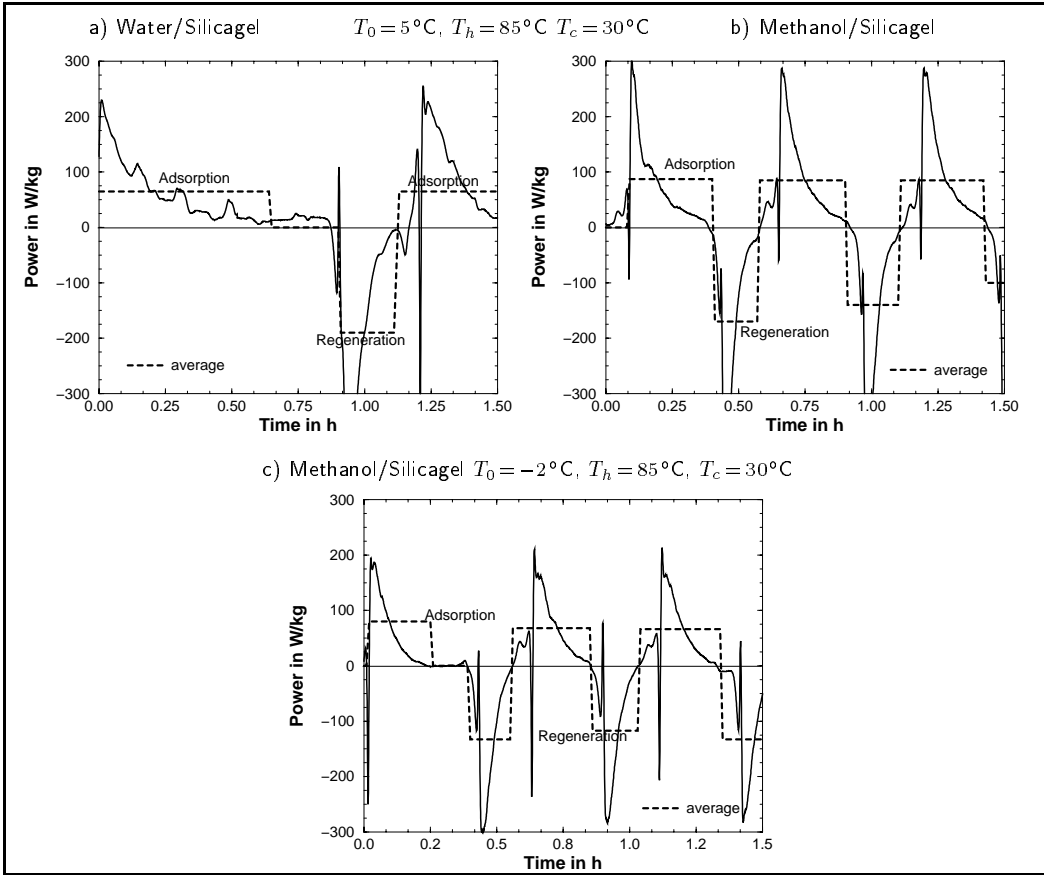


Fig. 8: Measured cooling power for a) water/silicagel and b) methanol/silicagel at  $T_0 = 5^\circ\text{C}$ ,  $T_h = 85^\circ\text{C}$ ,  $T_c = 30^\circ\text{C}$  and c) methanol/silicagel at  $T_0 = -2^\circ\text{C}$ ,  $T_h = 85^\circ\text{C}$ ,  $T_c = 30^\circ\text{C}$

## Comparison of Water and Methanol as Refrigerant

Operating with water and methanol at the same temperature levels the pressure at normal boiling is higher than for methanol due to its lower evaporation temperature. Nevertheless the resulting uptake is nearly the same as with water, as the higher pressure of methanol at normal boiling compensates a worse adsorption process due to the lower phase change energy of methanol.

The theoretical evaluation of the measurements have shown, that the measurements can confirm the theory. The uptake profile of a refrigerant/adsorbent-pair describes well the heat and mass transfer behavior, as shown by Sakoda [5]. The different characteristic times for the adsorption of methanol and water results from different mass transfer coefficients  $k_s a_p$  in equation [2].

More relevant for the technical application however is the power output of the chiller. In Fig. 8 curves for the transferred heating and cooling power using

water or methanol are displayed. These charts correspond to the theoretical curve, resulting from the product of uptake and specific heat of adsorption (equation 3). The small peaks e.g. at  $t = 0.1$  h and  $t = 0.45$  h are caused by the bypass operation, due to restrictions of the test facility. The peaks for negative power are caused by the regeneration phase, when energy is needed for desorption.

Whereas the amount of absorbed mass is nearly the same for both refrigerants, the resulting integral cooling power for the two refrigerants is different. This is caused by the different heat of vaporization and adsorption (Tab. 1). Methanol has about half of the latent heat for the phase change of water and thus the resulting turnover of energy is less. The integral energy absorbed during one cycle is higher for water, the adsorption process however takes nearly double the time (0.8 h for water, 0.3 h for methanol).

Like the energy required to heat and cool the heat exchanger and the silicagel between ad- and desorption is the same for both refrigerants. The lower amount of energy used for the phase change results in a lower COP.

### Operation below 0°C

According to the boiling point curve the evaporation pressure is reduced as well as the maximum uptake of the adsorbent. When lowering the boiling temperature  $T_0$  to -2°C the evaporation pressure is about  $p_0 = 20$  hPa and the maximal uptake is about 11.3% (Fig. 7b). The evaporation temperature effects only the maximal uptake, whereas the minimal uptake at regeneration is not influenced by the evaporation temperature. If possible, the regeneration temperature should be raised, to enlarge the amount of adsorbed refrigerant and thus to improve the performance data.

Without raising the firing water temperature  $T_H$  the resulting chiller power is reduced to an average value of about 10 W/kg Silicagel (Fig. 8c, Tab. 3).

### Adsorption Data of a Commercial System

For a prediction of the use of methanol/silicagel in a commercial application the results for water/silicagel of the test facility with the data of the commercial system are compared. Extrapolating the relation between test facility and commercial system for the working pair water/silicagel, informations for the use of methanol/silicagel can be achieved.

Comparing the specific power of a commercial system with the results of the test facility shows that the power density is only about 1/15 (Tab. 3). The COP for the commercial system at the selected point of operation ( $T_0 = 5^\circ\text{C}$ ,  $T_h = 85^\circ\text{C}$ ,  $T_c = 30^\circ\text{C}$ ) is about 0.58. The operation period for this two-chamber

Refrigerant	Test facility			Commercial System
	Water	Methanol		Water
Evaporator Temp.	5°C	5°C	-2°C	5°C
Transferred Energy	70 kJ	35 kJ	25 kJ	360 kJ
Cycle period	60 min	35 min	35 min	6 min
Mass of silicagel	0.6 kg	0.6 kg	0.6 kg	200 kg
Specific power	32 W/kg	27 W/kg	20 W/kg	300 W/kg

Table 3: Specific power density

system is about 6 min. The much higher power density of the commercial system is probably mainly reached by a silicagel with a faster sorption kinetic. If the silicagel has a higher mass transfer coefficient, adsorption and regeneration cycle takes less time and thus the resulting chiller power density is higher. It can be assumed, that similar to water with methanol as refrigerant a higher power density (200 W/kg) can be achieved.

## SUMMARY AND CONCLUSIONS

Due to the restrictions of the operation temperature level an adsorption chiller seems to be the most suitable cooling system for the mentioned solar-hybrid operated cold store. According to the investigations a commercially available system for air-conditioning applications can be modified for the operation at cooling temperature below the freezing point of water. Methanol instead of water can be used as refrigerant. A thermodynamic analysis basing on the characteristic curve of a commercial system and the material properties of the refrigerant is carried out. It figures out that because of the inferior thermodynamic properties and the lower operation temperature the efficiency will be significantly reduced. Experiments and calculations show, that the COP for a commercial adsorption cooling system will be about 30% when operating the system with methanol/silicagel at a chilled water temperature of  $T_0 = -2^\circ\text{C}$ , a heating water temperature of  $T_h = 85^\circ\text{C}$  and a condenser temperature of  $T_c = 30^\circ\text{C}$ . These conditions of operation are suitable for the application to the mentioned solar-hybrid adsorption cooling system.

The optimization of the design of the heat exchanger and the selection of silicagel is also of great importance. The dead mass ratio must be minimized and the heat transfer must be maximized to improve the energy efficiency. By accelerating the mass transfer into the silicagel bed the mass of absorbed refrigerant can be raised and thus the specific power density.

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