ADSORPTION REFRIGERATION - AN EFFICIENT WAY TO MAKE GOOD USE OF WASTE HEAT AND SOLAR ENERGY

R. Z. Wang[#] and R. G. Oliveira
Institute of Refrigeration and Cryogenics, Shanghai Jiao Tong University,
Shanghai, 200030, P.R. China
[#] E-mail: rzwang@sjtu.edu.cn - Tel/fax: +86-21-6293-3838

ABSTRACT

This paper presents the achievements in solid sorption refrigeration prototypes obtained since the interest in sorption systems was renewed at the end of the 1970s. The applications included are ice making and air conditioning. The latter includes not only cooling and heating, but also dehumidification by desiccant systems. The prototypes presented were designed to use waste heat or solar energy as the main heat sources. The waste heat could be from diesel engines or from power plants, in combined cooling, heating and power systems (CCHP). The current technology of adsorption solar powered icemakers allows a daily ice production of between 4 and 7 kg per m^2 of solar collector with a solar COP between 0.10 and 0.15. The silica gel-water chillers studied can be powered by hot water warmer than 55 °C. The COP is usually around 0.2 to 0.6, and in some commercially produced machines, the COP can be up to 0.7. The utilization of such chillers in CCHP systems, hospitals, buildings and grain depots are discussed. Despite their advantages, solid sorption systems still present some drawbacks such as low specific cooling power and COP. Thus, some techniques to overcome these problems are also contemplated, together with the perspectives for their broad commercialization.
Adsorption, Refrigeration, Heat Pump, Heat Management.

1. INTRODUCTION

The interest in adsorption systems started to increase, firstly due to the oil crisis in the 1970s that lead to a concern about the energy shortage, and then later, in the 1990s, because of ecological problems related to the use of CFCs and HCFCs as refrigerants. Such refrigerants, when released into the atmosphere, deplete the ozone layer and contribute to the greenhouse effect. Furthermore, with the increase of the energy consumption worldwide, it is becoming even more urgent to find ways of using the energy resources as efficiently as possible. Thus, machines that can recover waste heat at low temperature levels, such as adsorption machines, can be an interesting alternative for a wiser energy management.

The conventional adsorption cycle has been presented extensively in the literature [1-3] and it mainly includes two phases:

1) Adsorbent cooling with adsorption process, which results in refrigerant evaporation inside the evaporator and, thus, in the desired refrigeration effect. At this phase, the sensible heat and the adsorption heat are consumed by a cooling medium, which is usually water or air.

2) Adsorbent heating with desorption process, also called generation, which results in refrigerant condensation at the condenser and heat release into the environment. The heat necessary for the generation process can be supplied by a low-grade heat source, such as solar energy, waste heat, *etc*.

In comparison with mechanical vapour compression systems, adsorption systems have the benefits of energy saving if powered by waste heat or solar energy, simpler control, no vibration and lower operation costs. In comparison with liquid absorption systems, adsorption ones present the advantage of being able to be powered by a large range of heat source temperatures, starting at 50 °C and going up to 500 °C. Moreover, the latter kind of system does not need a liquid pump or rectifier for the refrigerant, does not present corrosion problems due to the working pairs normally used, and it is also less sensitive to shocks and to the installation position. These last two features make it suitable for applications in locomotives, busses, boats and spacecrafts.

Although adsorption systems present all the benefits listed above, they usually also have the drawbacks of low COP and low specific cooling power (SCP). However, these inconveniences can be overcome by the intensification of the heat and mass transfer properties in the adsorber, by increasing the adsorption properties of the working pairs and by a better heat management during the adsorption cycle. Thus, most research on this kind of system is related to the evaluation of the adsorption and physical-chemical properties of the working pairs [4-19], to the development of predictive models of their behaviour in different working conditions [20-33], and to the study of the different kinds of cycles [34-51]. Based on the results of these kinds of research, some prototypes were constructed and they had their performance evaluated in laboratory or in real applications.

This paper presents the results obtained with these prototypes and some adsorption machines already on the market, and shows the analyses of their advantages and their disadvantages.

The prototypes in question were designed to use waste heat or solar energy as the main heat sources. The applications in focus are ice making and air conditioning. The air conditioning systems comprise those with closed cycles and those with open cycles, such as in desiccant systems.

The alternatives already studied to increase the performance of the machines are also presented. They mainly include the use of advanced type sorption cycles to improve the internal heat management and heat transfer intensification within the adsorber to improve the SCP.

2. SOLAR POWERED ADSORPTION ICEMAKERS

Places with high insolation usually have a large demand for cooling to preserve food, drugs and vaccines, and much research has been devoted to develop machines that could employ solar energy efficiently for such purpose. The development of sorption refrigeration systems powered by solar energy emerged in the late 1970s following the pioneering work of Tchernev [52], who studied a basic solid sorption cycle with the working pair zeolite-water. Since then, a number of studies have been carried out, both numerically and experimentally, but the costs of these systems still make them non-competitive for commercialisation. Therefore, the focus of some research is placed on cost reduction and on the increase of the efficiency of the machines, and promising results have already been obtained.

Based on the results of a previous study [53], Pons and Guilleminot [54] concluded that the solid sorption systems could be the basis for efficient solar powered refrigerators, and they developed a prototype with the pair activated carbon-methanol.

This machine produced almost 6 kg of ice per m^2 of solar panel when the insolation was about 20 MJ day^{-1}, with a solar COP of 0.12. This rate of ice production remains one of the highest obtained by a solar powered icemaker.

Critoph [55] mentioned a solar vaccine refrigerator studied in his laboratory in the early 1990s [56]. Such machine, shown in Fig. 1, could keep the cold box at 0 °C during the daytime, after one adsorption cycle performed during the previous night. According to this author, although the COP and ice production of this machine, that used the pair activated carbon-ammonia, were smaller than those produced by a machine with the pair activated carbon-methanol, the former is less sensitive to small leakages, which makes it more reliable to be applied in remote areas where the maintenance is not readily available.

Fig. 1. Solar cold box for vaccine preservation [55].

Li et al. [57] performed experiments with the solar ice maker that is shown schematically in Fig. 2. This icemaker that used carbon-methanol as working pair had a COP ranging from 0.12 to 0.14, and produced between 5 and 6 kg of ice per m^2 of collector. Analysing the temperature gradient within the adsorbent bed, the authors concluded that in order to improve the performance of this system, the heat transfer properties of the adsorber needed to be enhanced. This could be achieved by increasing the number of fins or using consolidated adsorbent.
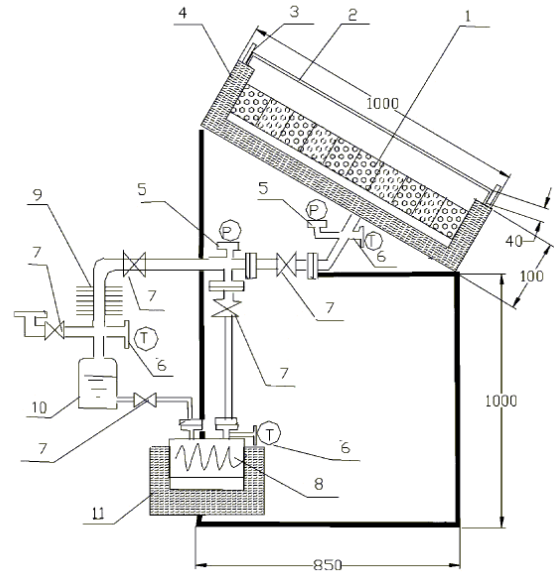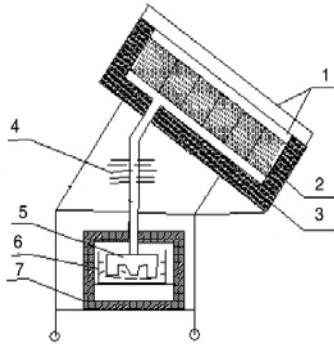

Fig. 2. Scheme of the solar adsorption icemaker: 1) adsorbent bed; 2) glass cover; 3) damper; 4) insulation; 5) pressure gauge; 6) temperature gauges; 7) valves; 8) evaporator; 9) condenser; 10) refrigerant reservoir; 11) ice box [57].

Based on the previous prototype, Li et al. [58] developed a simpler solar powered icemaker without valves, as shown in Fig. 3. The authors decided to produce the adsorber from stainless steel, instead of cooper or aluminium alloys. This was done since according to experiments done by Hu [59], at temperatures higher than 110 °C, methanol will decompose into dimethyl-ether, which would reduce the efficiency of the system with the time.

The adsorber was placed inside an insulated case, which was covered by two transparent plastic fibre sheets. This kind of plastic fibre is more suitable to cover the adsorber than glass because its permeability to solar radiation is higher. To ensure better heat transfer between the front side of the solar collector and the adsorbent, several fins (also made of stainless steel) were placed inside the adsorber. The distance between these fins was approximately 0.1 m and the thickness of the adsorbent layer was 0.04 m. According to the authors, these dimensions were decided according to previous experimental results and optimisation studies.

The experiments with this prototype were performed both under indoor (insolation simulated with quartz lamp) and under outdoor conditions. Under indoor conditions, with an insolation from 17 to 20 MJm^{-2}, the ice production was between 6.0 and 7.0 kg per m^2 and the COP between 0.13 and 0.15. Under

outdoor conditions (insolation from 16 to 18 MJm^{-2}), the system could produce 4.0 kg of ice per m^2 with a COP of about 0.12. Based on the results with this prototype, two new prototypes were developed, where the adsorber wall thickness was reduced. These prototypes could produce between 4.0 and 5.0 kg of ice per m^2, with a COP from about 0.12 to 0.14, when the solar radiation was between 18 and 22 MJm^{-2}. The cost of such a machine was estimated to be no more than US$ 250 per m^2 of solar panel.
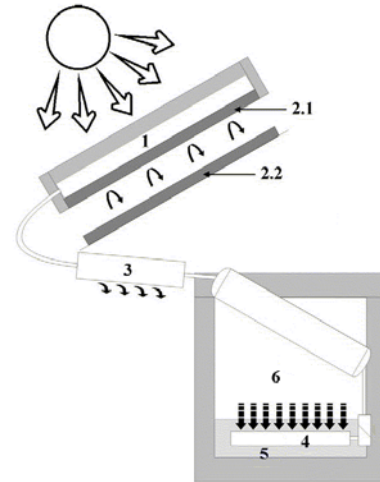

(a) Scheme of the solar powered icemaker.


(b) Photo of the solar powered icemaker.

Fig. 3. Solar powered icemaker without valves. 1) cover plate; 2) adsorbent bed; 3) insulation; 4) condenser; 5) evaporator; 6) water tank; 7) cold box [58].

An adsorption icemaker, also with the pair activated carbon-methanol, was tested in Burkina Faso by Buchter *et al.* [60]. The results of this prototype were compared to those obtained by Boubakri *et al.* [61,62] in Morocco, with a similar system, which was commercially produced in the 1980s by the French company BLM. The main difference between those systems is the presence of ventilation dampers in the former (as can be seen in Fig. 4), which were open during nighttime to improve the cooling of the adsorbent bed. The machine tested in Burkina Faso presented a cooling performance about 35 % higher than that of the machine tested in Morocco. The COP of the former machine ranged from 0.09 to 0.13 when the insolation ranged from 22 to 25 MJ m^{-2}. In this system, the ice produced during the adsorption time was not removed from the cold box, and it was used to keep the box at about 5 °C during daytime.

Fig. 4. Scheme of the solar powered refrigerator: 1) solar collector/adsorber; 2) ventilation dampers (.1) closed, (.2) open; 3) condenser; 4) evaporator; 5) ice storage; 6) cold box [60].

Hildbrand *et al.* [63] developed an adsorption icemaker in which water was used as refrigerant and the ice was produced within the evaporator. The adsorbent was silica gel and the total solar collector area was 2 m^2. The scheme of this machine is presented in Fig. 5. The experiments were carried out over a period of 68 days and showed the considerable influence of the environmental conditions (insolation and outdoor temperature) on the performance of the system. For insolation higher than 20 MJm^{-2}, the COP was between 0.12 and 0.23, when the mean outdoor temperature was between 12 and 25 °C. COPs higher than 0.15 were generally obtained with outdoor temperatures below 20 °C.
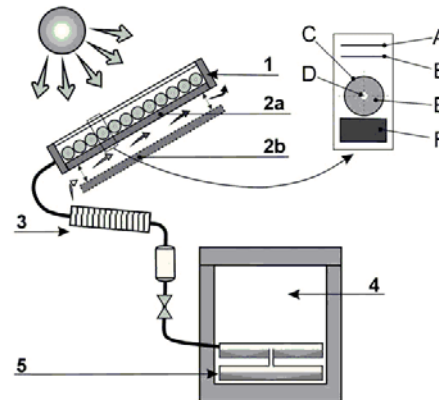
Fig. 5. Solar collector/adsorber. 1) with detail: glass cover (A); Teflon film (B); tube covered with selective surface (C); central tube for vapour transport (D); silica gel bed (E); thermal insulation (F); 2) ventilation dampers (a - closed – b - open); 3) condenser; 4) cold box; 5) evaporator and ice storage [63].

All the experiments were performed employing a constant load (4.1 MJday^{-1}) inside the cold box. The temperature of the evaporator was kept constant during a period of 30 days, where

the total insolation received by the system was 923 MJ and the thermal loss for the ambient was estimated in 26 MJ. From these values, the authors calculated an average COP of 0.16. The daily ice production was not measured because the ice was formed inside the evaporator. If thermal losses in the ice production are neglected, a cooling charge of about 440 kJ can be assumed to produce 1 kg of ice; therefore, this system would have a daily ice production of 4.7 kg per m^2 of solar panel.

An innovative modular icemaker was tested by Khattab [64]. It placed the adsorbent in a glass container, which was positioned between reflector panels, as shown in Fig. 6. The author tested these panels at different inclinations to assess which configuration could allow the adsorber to reach higher temperatures. The area of each panel was 0.04 m^2, and the diameter of the circular adsorber was 0.2 m^2.

In order to improve the thermal properties of the adsorbent bed, four types of bed techniques were proposed:
i) black metallic meshes on both faces of the glass adsorber and granular carbon inside;
ii) black metallic plates on both faces of the glass adsorber and granular carbon inside;
iii) granular carbon mixed with small pieces of blackened steel;
iv) granular carbon bonded with small pieces of blackened steel.
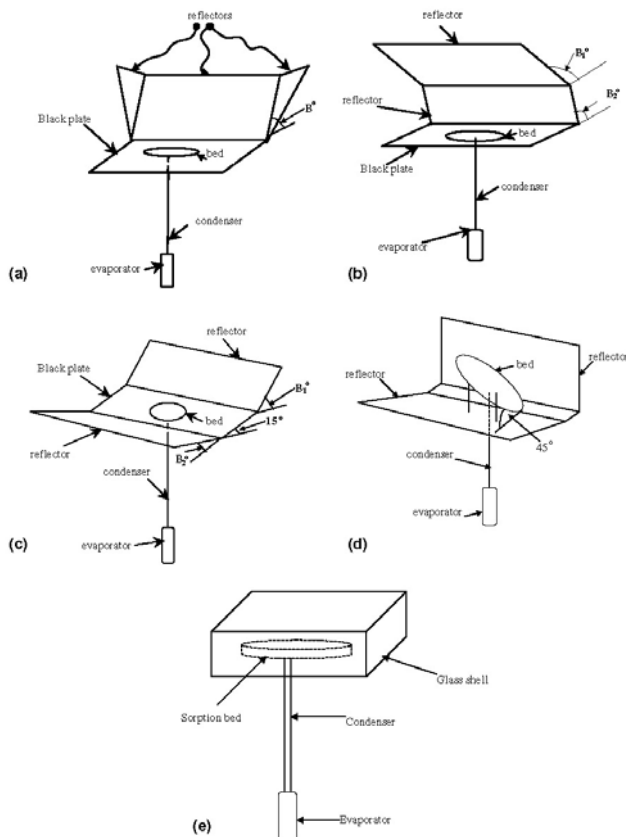
Fig. 6. Reflector arrangements [64].

According to the author, the proposed design has several advantages over the conventional design because each module can be considered as a single refrigeration unit with simple structure, low cost and high solar energy concentration, due to the utilization of plane reflectors.

The glass adsorber allows the adsorbent to receive the solar energy directly on both sides; thus, the effectiveness in the solar energy absorption is enhanced. As the adsorbent is uniformly heated during daytime, there is no need for insulation, which allows for effective cooling in nighttime.

Due to the construction, the adsorber, the condenser and the evaporator are inside a single glass unit, which eliminates possible places for air infiltration, and reduces the necessity for maintenance.

The configuration with granular carbon bonded with blackened steel and using the reflector panel position type (c) had a COP of 0.16 and a daily ice production of 9.4 kg per m^2 of adsorber when the insolation was about 20 MJm^{-2} and the average outdoor temperature was 29 °C. Under winter conditions with insolation of 17 MJm^{-2} and an average outdoor temperature of 20 °C, the COP obtained was 0.14 with a daily ice production of 6.9 kg per m^2.

Oliveira [65] tested an adsorption icemaker with refrigerant mass recovery process that had a daily ice production of 1.2 and 1.6 kg per kg of adsorbent when the generating temperatures were 75 °C and 85 °C, respectively. The COP, in both cases, was about 0.08. The adsorbers were heated by a thermal fluid, and a flat plate collector could be employed to produce fluid at temperatures close to 85 °C. Higher ice production could be expected if the heat transfer in the evaporator was enhanced and if the time length of the vapour recovery was shortened. The time chosen in the experiments, due to experimental difficulties, was close to 20 % of the cycle time, although the greatest amount of mass recovery happened in the first minute of this process.

A different approach to increase the overall efficiency of the adsorption icemaker was studied by Wang et al. [66], who joined a solar water heater and an icemaker in the same machine. This machine, shown in Fig. 7, used the working pair activated carbon-methanol and had 2 m^2 of evacuated tube collectors to warm 60 kg of water up to 90 °C. The daily ice production was about 10 kg when the insolation was about 22 MJm^{-2}.
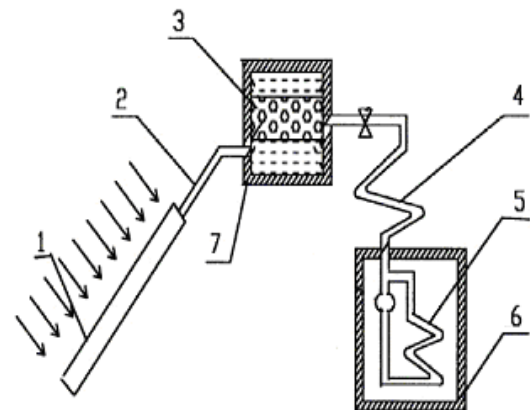

Fig. 7. Scheme of the solar powered water heater and refrigerator. 1) Solar collector; 2) water pipe; 3) adsorber; 4) condenser; 5) evaporator; 6) refrigerator (with cold storage); 7) hot water storage tank [66].

This system is a combination of solar powered water heating and adsorption refrigeration, where the adsorber remains

immersed in the solar heated water in a storage tank while performing the generation process (T_{a2} to T_{g2} in Fig. 8). During the night, the hot water can be used for domestic or sanitary purposes, and as it is drained from the storage tank, the tank is refilled with ambient temperature water at T_0. This water reduces the temperature of the adsorber (T_{g2} to T_{a1}), which adsorbs refrigerant from the evaporator and starts the ice production (T_{a1} to T_{a2}). The sensible heat and adsorption heat from the adsorber are then, transferred to the water in the tank, which causes an increase of about 5 °C in the temperature of the water (T_0 to T_{a2}). This way, what would be waste heat is converted into useful heat by this heat recovery process.
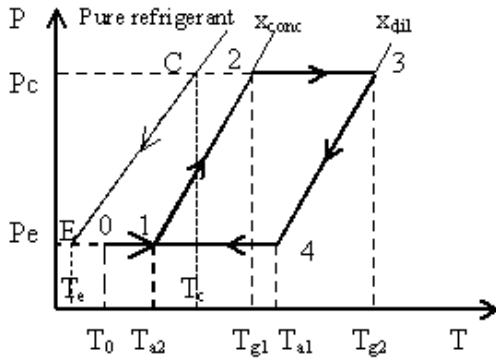
Fig. 8. Clapeyron diagram for combined water heating and sorption refrigeration system with heat recovery.

A similar system was studied by Wang *et al.* [67] who assumed that the 4 kg of ice produced by the adsorption system could be used to keep a 100 L cold box at 5 °C or below for at least 55 hours if the heat input on the system was between 50 and 55 MJ. Under these conditions, the daily production of hot water would be 120 kg. When the provided input energy was about 40 MJ, the temperature in the cold box could be kept below 4 °C for at least 24 hours.

3. SOLAR POWERED ADSORPTION AIR CONDITIONERS

In many countries during summer, the demand for electricity greatly increases due to the intense use of air conditioners. Problems, like blackouts, can occur if the capacity of the power plants is not sufficient to meet this demand, especially during peak hours. As this period usually coincide with the higher insolation hours, the use of solar powered air conditioners seems to be an attractive solution.

At the end of the 1980s, Grenier *et al.* [68] presented a solar adsorption air conditioning system that had 20 m² of solar panel and used the working pair zeolite-water. This system, shown in Fig. 9, was designed to refrigerate a 12 m³ room for food preservation. When the insolation received by the solar collectors was about 22 MJm⁻², the cold room could store 1,000 kg of vegetables with a rotation of 130 kg per day for a temperature difference of 20°C between the ambient outside and the cold room. The COP, in this case, was 0.10.

Saha *et al.* [69] experimentally investigated a double-stage, four-bed, non-regenerative adsorption chiller that could be powered by solar/waste heat sources at between 50 and 70 °C.

The prototype studied produced cold water at 10 °C and had a cooling power of 3.2 kW with a COP of 0.36 when the heating source and sink had a temperature of 55 and 30 °C, respectively. Flat plate collectors could easily produce hot water to regenerate the adsorbent of the chiller at these levels of temperature.

Fig. 9. Cold storage room.

An adsorption air conditioning system was developed by Wang *et al.* [70] to be powered by heat sources with temperatures close to 100 °C. Evacuated tube collectors could be used to supply hot water at this level of temperature. The system, which the scheme is shown in Fig. 10, had two adsorbers with 26 kg of carbon inside each one and used methanol as refrigerant.
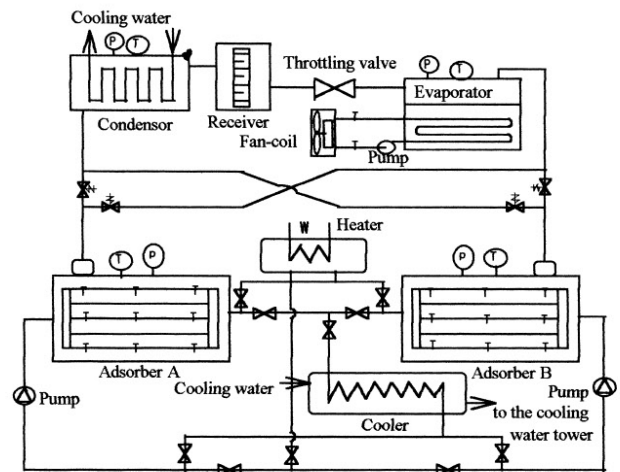

Fig. 10. Scheme of the adsorption air conditioner [70].

The COP and the SCP of this system were significantly influenced by the cycle time. The operation of the system with a cycle time of 30 minutes leads to a COP of 0.15 and a cooling power of 3.84 kW while operation with a cycle time of 60 minutes leads to a COP of 0.21 and cooling power of 3.03 kW. In both situations, the evaporation temperature was close to 6 °C. To improve the performance of the system, the authors changed the adsorbers, keeping the same charge of carbon, and used a tube and plate heat exchanger being the carbon placed outside the tubes, between the plates. With this new design, the

COP obtained was 0.4 and the cooling power was 3.80 kW. The experimental conditions in this case were: a heat source temperature of 100 °C, an evaporation temperature of 10 °C, a condensing temperature of 24 °C and a cycle time of 50 minutes.

Liu *et al.* [71], developed an adsorption chiller with the pair silica gel-water that had no refrigerant valves. This feature reduces the cost of the chiller, and makes it more reliable as there are fewer moving parts that could lead to air infiltration. The sorption bed of such a chiller could be regenerated by hot water at between 75 and 90 °C.

The whole chiller contains 52.8 kg of silica gel divided between two adsorbent beds, which operate out of phase and, thus, produce constant cooling. Experiments with the first prototype showed that a cooling power of 3.56 kW and a COP of 0.26 could be obtained when the mass and heat recovery processes are employed under the follow operation conditions: an evaporation temperature of 7 °C, a heat sink temperature of 28 °C, and a heat source temperature of 85 °C. A scheme of this chiller integrated into a solar water heater is shown in Fig. 11.
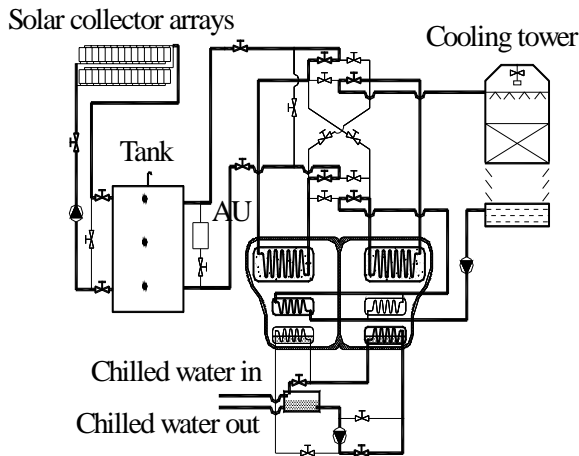
**Fig. 11. Scheme of the silica gel-water adsorption chiller powered by the solar water heater.**

To enhance the performance of the chiller, the research team developed a new prototype, show in Fig. 12, with some improvements. The new prototype had less non-continuous and movable pieces to reduce the number of possible places for inward air leakage. The condenser was changed to avoid undesirable refrigerant evaporation that occurred inside this device during the operation of the first machine. The configuration of the adsorber was changed to improve the heat and mass transfer. Although there was some difficulty in testing both prototypes under the same operation conditions, the second prototype proved to have better performance than the first one. The second prototype had a cooling power and a COP about 34 % and 28 % higher than the first one, even if the bed of the former was regenerated by lower generation temperature. Experiments performed at a generation temperature of 80 °C and an evaporation temperature of 13 °C showed that the COP and the cooling power of this new system could reach 0.5 and 9.0 kW, respectively.
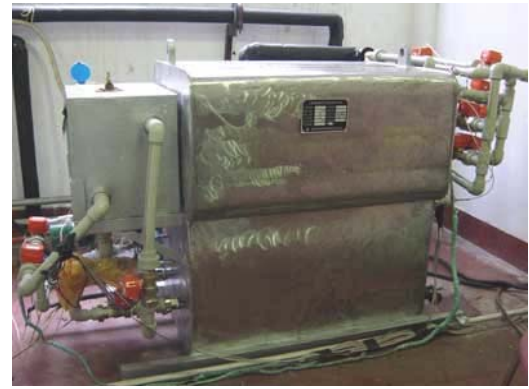
Fig. 12. The 2nd generation of the adsorption chiller developed in the SJTU [71].

Xia *et al.* [72] applied for a patent of a silica gel-water adsorption chiller driven by a low temperature heat source. This chiller has two identical chambers and a second stage evaporator with methanol as working fluid. Each chamber contains one adsorber, one condenser and one evaporator (the first stage evaporator). There is also a mass recovery tube between the two chambers.

Such a chiller is used to cool a grain depot in the Jiangsu Province, in China. The whole refrigeration system, shown in Fig. 13, mainly consists of four subsystems, namely, solar powered water heating unit, adsorption chiller, cooling tower and fan coil unit. The solar powered water-heating unit includes almost 50 m^2 of evacuated tube collectors, a water pump and a hot water storage tank.
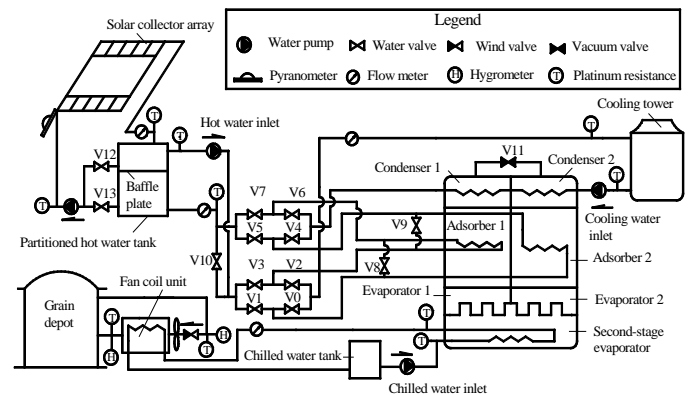

Fig. 13. Scheme of the solar powered adsorption chiller used for cooling a grain depot.

The heating unit produces hot water that regenerates the adsorption bed of the chiller. The cooling tower is used to remove heat from the condensers and from the adsorbers. The cooling effect obtained during the adsorption phase of the chiller was transferred to the grain depot through the fan coil unit. The available hot water provided by the solar collectors had a temperature between 60 and 90 °C. Field measurements showed that under a daily solar radiation between 16 and 21 MJm^{-2}, the chiller could supply cold air with temperatures from 14 to 22 °C.

Experiments performed when hot water at 85 °C was used to drive the chiller, resulted in a cooling power close to 4.96 kW,

with the corresponding cycle COP around 0.32. When the hot water temperature was 65 °C, the cooling power and cycle COP were 2.97 kW and 0.23, respectively. These values indicate that the solar collectors can effectively drive the adsorption chiller.

As can be seen in Fig. 14, the chilled water inlet temperatures greatly affect both the average cooling power and the cycle COP of the chiller. Thus, when ever possible, the highest inlet water temperature should be used to ensure high performance of the chiller.
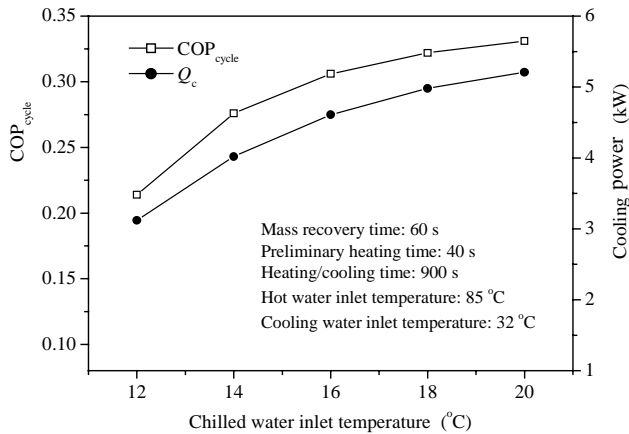
Fig. 14. Variations of cycle COP and cooling power with chilled water inlet temperature.

Two chillers similar to the one described previously, but with a higher nominal capacity are used in the air conditioning system of a "green" building located in the Shanghai Research Institute of Building Science. The chillers, which are shown in Fig. 15, were installed in the equipment room located on the top floor of the building and operate from 9:30 AM to 4:30 PM. Experiments performed when the daily solar radiation was 19.2 MJm^{-2}, showed that the chillers had an average cooling power of about 12 kW, with corresponding cycle and solar COP of 0.28 and 0.09, respectively. The silica gel beds of these chillers were regenerated by hot water at 65 °C, produced in 170 m^2 of U-type evacuated tube collectors. The average efficiency of the solar collectors was about 36%. If the hot water supplied to the chiller reaches about 85 °C, which could be expected on sunny summer days, the cooling power of these chillers could be close to 15 kW.

Fig. 15. (a)Shanghai Green Building; (b) adsorption chiller powered by solar energy.

Nuñez et al. [73] developed and tested a silica gel-water adsorption chiller with nominal cooling power of 3.5 kW. It had two adsorbers filled, each one, with 35 kg of adsorbent. The chiller operated at generation temperatures between 75 and 95 °C, heat sink temperatures between 25 and 35 °C, and evaporation temperature ranging from 10 to 20 °C. The COP varied from 0.4 to 0.6 according to the experimental condition. The authors compared the performance of this chiller to the performance of the Nishiyodo NAK 20/70 adsorption chiller and to the Yasaky WFS SC-10 absorption chiller. The figures of merit compared were the COP and the cooling power density at different reduced temperatures. This temperature was defined as the ratio between the adsorber-evaporator temperature gap and the adsorber-condenser temperature gap during the adsorption and desorption phases, respectively.

At reduced temperatures below 0.35, the absorption chiller produced the highest COP (about 0.7), and it was followed by the Nishiyodo adsorption chiller (COP of 0.65) and by the experimental prototype chiller (COP of 0.60). The cooling power density of the absorption chiller at this reduced temperature was much higher than that of the adsorption chillers (30 kWm^{-3} and 15 kWm^{-3} for the absorption chiller and for the prototype, respectively), but at higher reduced temperature, the prototype and the absorption chiller produced almost the same cooling power density (about 15 kWm^{-3}). These results indicate that the cooling power of adsorption chiller is more constant than that of the absorption chiller with respect to the variation of the working temperatures.

Restuccia et al. [74] developed an adsorption chiller that employed silica gel impregnated with $CaCl_2$ as sorption material. This kind of adsorbent was chosen due to its high sorption ability (up to 0.7 kg of water per kg of dry sorbent) and due to the fact that most of the water content can be desorbed at generation temperatures between 90 and 100 °C. When the condensation temperature was 35 °C, the COP of the chiller was close to 0.6 in the range of generation temperatures from 85 to 95 °C, but it varied between 0.3 and 0.4 when the condensation temperature was 40 °C. The evaporation temperature during these experiments was 10 °C. The SCP was 20 W kg^{-1} when the generation temperature was 95 °C and the condensing temperature was 40 °C.

Another kind of solar powered air conditioner employs open adsorption systems, instead of closed ones. These systems are called open because the refrigerant, which is water from the air, is released into the atmosphere after the desorption process.

Ismail et al. [75] studied a system with silica gel designed to reduce the absolute humidity and enthalpy of the air used to cool grains. In such a system, the air passed through two silica gel beds and two heat exchangers to provide dry air during the night to a grain storage room. During the daytime, the silica gel beds were regenerated by ambient air with low relative humidity, and which was heated by solar energy in the heat exchangers. The utilization of this system could keep the temperature of the grain at about 16 °C, while this temperature would be closer to 21 °C without the system. The COP, based only on the electricity supplied to the system, was greatly influenced by the airflow rate, and it ranged from 3.9 to 30.3 for an airflow rate between 0.065 kg s^{-1} and 0.021 kg s^{-1}. According to the authors, the main reason for theses differences in the COP is the non linear resistance to the airflow through the system, which greatly increases the power required by the fan to produce higher flow rates in comparison to that required to produce lower ones.

Toruwa *et al.* [76] also studied a system, which is shown in Fig. 16, designed to provide conditioned air for grain storage. The system used solid compound desiccant comprised by a mixture of bentonite, $CaCl_2$, vermiculite and cement with the mass ratio of 6:1:2:1. The compound desiccant was placed inside a 0.9 m^2 flat plate collector. The dehumidified air, with 40 % reduced relative humidity, could be produced continually during nighttime at the rate of 2 m^{3}min^{-1}. During the daytime, the desiccant material was regenerated inside the collector, by an insolation around 19.5 MJm^{-2}.
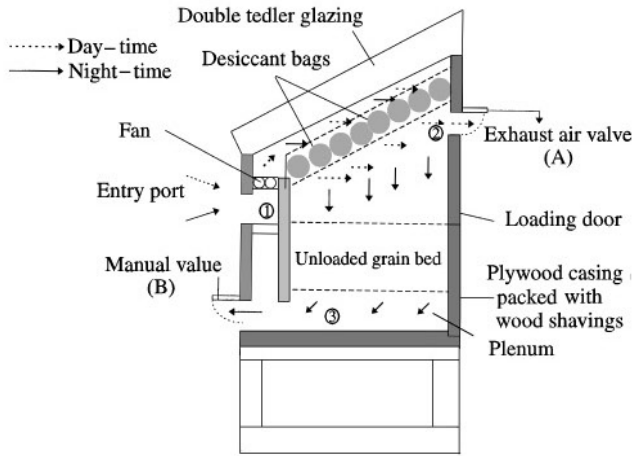
Fig. 16. Prototype of integrated desiccant/collector dehumidifier. (1, 2, 3) thermocouples [76].

Desiccant systems can also be used to improve the performance of evaporative cooling systems. A ventilation system for evaporative cooling with a desiccant wheel regenerated by solar energy is shown in Fig. 17. The evaporative cooling produces the cooling effect, however this effect is increased due to the dehumidification of the air by the sorbent. Such a system was studied by Henning *et al.* [77] and could produce inlet room air at 19 °C when the ambient temperature was as about 31 °C. The solar energy used for the regeneration of the sorbent was close to 76 % of the total input energy, and the COP of the system was 0.6.
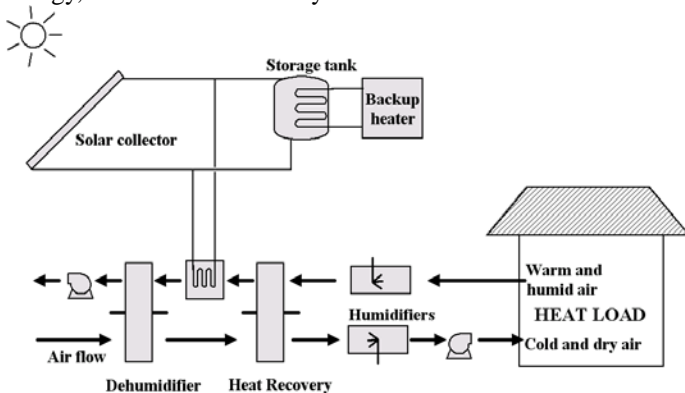

Fig. 17. Scheme of solar powered desiccant cooling system with backup heater.

The combination of desiccant wheel with the conventional vapour compression chiller can also increase the efficiency of the latter. This happens because the thermal driven sorption

wheel does the removal of the latent load and the chiller just does the removal of the sensible load. In such a situation, the chiller can work at evaporation temperatures close to 15 °C, instead of the usual 5 °C, which increases its efficiency.

Lu and Yan [78] studied another kind of open sorption system for air dehumidification and that could be regenerated by solar energy. This system identified as solar desiccant enhanced radiative cooling (SDERC), used silica gel as adsorbent. It was installed on the ceiling and sidewalls, as shown in Fig. 18, of the Building 64 in the Industrial Technology Research Institute, in Taiwan. The sorption panels placed on the ceiling and sidewalls covered an area of 6.7 and 4.5 m^2, respectively, and alternate their generation and adsorption phases to constantly produce dehumidified air.
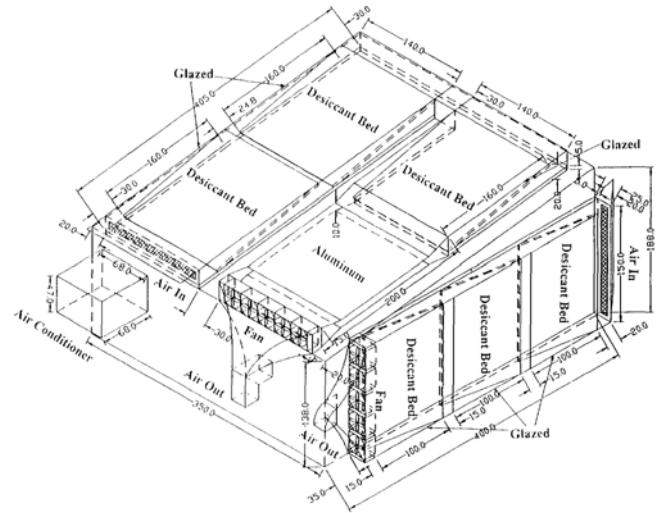
Fig. 18. Scheme of SDERC [78].

The dehumidification performance of the system greatly changes during the day, due to the different working conditions of the beds. The authors estimated that a mechanical compression air conditioning system would have the consumption of energy about 9 to almost 25 times higher than that of the studied system to perform a similar nighttime dehumidification. According to the authors, it is possible to save almost US$850 per year with the utilization of this system instead of the one with mechanical compression, provided that the electricity price is US$0.115 per kWh.

Apart from the presented studies from the scientific literature, the European project Climasol [79] presented examples of buildings that already use solar powered sorption air conditioners. The examples include applications of solid sorption chillers and solid desiccant systems. Some of the chillers were installed in a university hospital located in Freiburg, Germany, and in the cosmetic company Sarantis S.A., in Greece, while some of the solid desiccant systems were installed in the Chamber of Commerce in Freiburg, and in the Renewable Energies Department, in Lisbon.

The system in the university hospital has 230 m^2 of evacuated tube collectors with that produce hot water used to power an adsorption chiller with a 70 kW cooling power, during summer, or to pre-heat the air during winter. The COP of this chiller is about 0.6 and the efficiency of the solar collectors is 32 %. € 353,000 was invested in this system, that was

installed in 1999, and the annual operation cost is about € 12,000.

The system located in the cosmetic company uses 2,700 m^2 of flat plate collectors to produce hot water with a temperature of 70 to 75 °C. This water is used in during the summer to power two adsorption chillers with 350 kW of cooling power each. The COP of these chillers is about 0.6. In winter, the hot water is used for heating purposes inside the buildings. The area managed by the air conditioning system is 22,000 m^2 (130,000 m^3). There are also three mechanical compression chillers with 350 kW of power to supply the cooling demand in the peak hours. The solar energy used to drive the chillers is around 66 % of the total input energy, and oil burners are employed as heat source during periods of low insolation.

The cost of the machinery was € 1,300,000 and it could reduce the CO_2 emissions by about 5,100 tons year^{-1}.

In the Chamber of Commerce, in Freiburg, a 100 m^2 solar heated desiccant panel was installed to provide 60 kW of cooling. This system cools and pre-heats the air during summer and winter, respectively, of two rooms that have a total volume of 815 m^3. The investment in the system was €210,000. It was estimated that the utilization of this system could save around 30,000 kWh year^{-1} and avoid 8.8 tons year^{-1} of CO_2 emissions.

The air conditioning of the offices on the first floor of the Renewable Energies Department, in Lisbon, is performed by a desiccant system which cost was €75,000. Such a system can provide 36 kW of cooling with a COP of about 0.6. The solar energy used is about 44 % of the total energy input and the installed area of the flat plate collector is 48 m^2. The reduction in CO_2 emission with the utilization of this system was estimated to be about 3.5 tons year^{-1}, and the energy savings to be around 7,000 kWh year^{-1}.

4. ADSORPTION ICEMAKERS DRIVEN BY EXHAUST GASES

The efficiency of diesel engines is about 35 %, and in the operation of water-cooled engines, about 35 and 30% of the input energy is wasted in the coolant and exhaust gases, respectively [80]. Thus, recovering the waste heat can improve the energy management where such engines are employed. The use of this heat to regenerate the bed of adsorption systems is one of the alternatives to increase the overall efficiency of the diesel engine.

The mechanical vapour compression system is currently the most available technology nowadays for refrigeration purposes on fishing boats, but it has certain drawbacks such as the increase of fuel consumption on the boats, because some extra energy is needed to drive the compressor. Fishing boats are generally powered by diesel engines, and the employment of adsorption refrigeration systems instead of mechanical compression ones, could reduce their fuel consumption.

Wang et al. [81] developed an adsorption system in which the sorption beds could be regenerated by using exhaust gases of diesel engines. This system was designed for ice production, and the working pair employed was activated carbon and methanol. The exhaust gases holding a temperature of about 500 °C heated water in a heat exchanger and this water was used to heat the adsorbent at the generation phase. The temperature of the hot water was adjusted to always be lower

than 120 °C, because methanol, when in contact with activated carbon, is not stable at temperatures higher than this. The authors used solidified adsorbent, which is shown in Fig. 19, instead of granular one because of the difference in the heat transfer coefficient of these two materials (99 and 25 $Wm^{-2}K^{-1}$, respectively). Although the heat transfer performance of the solidified adsorbent was superior to that of the granular one, the mass transfer was inferior due to its low permeability. The authors stressed the importance of refrigerant flow channels inside the adsorbent to ensure that the rates of desorption and adsorption would not be influenced by the low permeability.
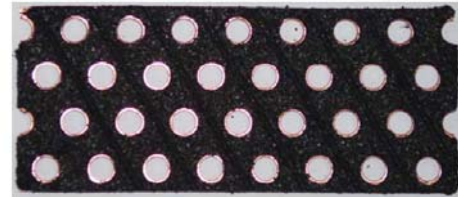

Fig. 19. Consolidated carbon block.

The experiments with this prototype were performed with and without refrigerant mass recovery. The mass recovery proved to increase the ice production by 11%. With a cycle time of 72 minutes and an evaporation temperature of –11 °C, the specific cooling power was 16.8 Wkg^{-1} and the COP was 0.12.

The consolidated carbon block was also used in a prototype developed by Wang and Wang [82]. The experiments with this machine employed heat and mass recovery processes to increase the SCP and the COP. An oil burner simulated the heat from the exhaust gases of a diesel engine. The system achieved a SCP of 27 Wkg^{-1} with a COP of 0.18, which resulted in a flake ice production from 18 to 20 kg h^{-1} at –7 °C. The Fig. 20 shows a photo of the prototype producing flake ice.
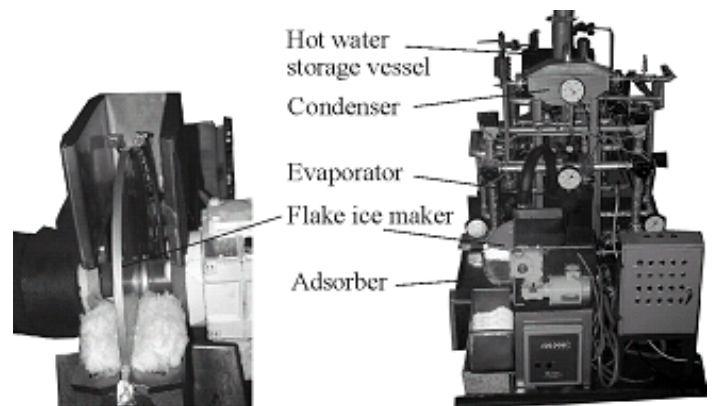

Fig. 20. Adsorption icemaker during ice production.

Tamainot-Telto and Critoph [83] developed an adsorption system with consolidated carbon block, and utilized ammonia as refrigerant. This system presented a SCP of 35 Wkg^{-1} and a COP of 0.10 when the evaporation temperature was –17 °C, the condensing temperature was 25 °C and the generation temperature was 105 °C. Assuming that this carbon had a density of 713 kg m^{-3}, this system could have a cooling power density close to 24.9 kWm^{-3}. The authors mention that the utilization of higher generation temperature and heat recovery

process could lead to higher SCP and COP.

Wang *et al.* [84] compared the performance of an adsorption system using different working pairs to identify the most suitable pair for adsorption ice making on fishing boats. The pairs compared were: 1) Activated carbon and methanol; 2) $CaCl_2$ and ammonia; 3) compound adsorbent (80 % $CaCl_2$ plus 20 % activated carbon) and ammonia. The pair activated carbon-methanol was that from Wang *et al.* [81]. In the experiment with the pair $CaCl_2$ and ammonia, the authors measured the adsorbed mass of refrigerant at an evaporation temperature of –15 °C for different expansion ratios (void volume per filled volume of dry salt) and calculated the expected cooling capacity. The expansion ratio that produced the higher cooling capacity was 2:1. The cooling capacity was about 889 kJkg^{-1}, and the cooling density was 185 MJm^{-3}. The value obtained for the cooling density includes not only the volume occupied by the dry salt but also, the void volume necessary for its expansion.

The compound adsorbent was tested in granular and consolidated form. The granular form presented attenuation in the adsorption performance. Based on the results of their experiments, the authors mentioned that a moderate agglomeration of the salt during the adsorption process is desirable to keep the adsorption properties stable on successive adsorption cycles, and this agglomeration was not observed with the granular compound.

To promote the desired agglomeration, the authors mixed the compound with cement and produced a consolidated adsorbent. This compound presented stable adsorption performance after several adsorption phases and higher packing density. It could produce a cooling capacity of about 660 kJkg^{-1}, and a cooling density of 254 MJm^{-3}, when the evaporation temperature was –15 °C. Although the cooling capacity obtained with the consolidated compound was smaller than that obtained with $CaCl_2$, the cooling density was about 38% higher. The increase in the cooling density happened because the packing density of the consolidated compound is higher than that of the $CaCl_2$ (360 and 207 kg m^{-3}, respectively). $CaCl_2$ has low packing density because a high expansion space must be used inside the adsorber, as the $CaCl_2.8NH_3$ has a molar volume 4 times higher than that of the dry salt. Thus, for an application where a reduced volume is more important than a reduced mass, the consolidated compound is preferable.

These authors estimated that for a 60 minutes cycle, the utilization of consolidated composite compound and $CaCl_2$ would lead to a cooling power of about 20.3 and 14.8 kW, respectively, if they were placed in an adsorber with 0.29 m^3 of useful volume. This volume was chosen to allow a comparison with the system developed by Wang *et al.* [81], and which had a cooling power of 2.0 kW.

The same group from the previous work has achieved more progress recently with heat-powered adsorption icemakers. The new research show that split heat pipes can be successfully used in adsorption systems to heat and cool the adsorbers. This arrangement avoids the direct contact between the adsorber and the exhaust gases or the seawater. Furthermore, a significant increase of the COP and the SCP was noticed in the new system, and these results are presented in section seven of this paper.

5. ADSORPTION AIR CONDITIONERS DRIVEN BY EXHAUST GASES

Air conditioning on vehicles could be another reasonable application for adsorption systems powered by exhaust gases. The vehicles more suitable for this kind of air conditioner are buses and locomotives, as adsorption systems usually still have large volume and mass.

Zhang [80] studied an adsorption air conditioning system that could have the sorption beds regenerated by the exhaust gases of a bus. The adsorber consist of two concentric pipes, and the exhaust gases or the cooling air flowed through the inner pipe, to release or remove heat from the adsorbent, respectively. The adsorbent (zeolite) was placed between the inner and the outer pipe. Fins were attached to the inner pipe to increase the heat transfer between the fluids and the adsorbent, and water was used as refrigerant.

The COP found was 0.38 and the SCP was 25.7 Wkg^{-1}. The author also calculated the coefficient of waste heat cooling (WCOP), which takes into account the potential waste heat that can be recovered to produce the cooling effect, without the gas reaches the dew point. The value of WCOP found for this system was 0.31. This author suggested that the WCOP is more suitable than the COP to identify which cooling capacity could be produced from the exhaust gases of diesel engines, because in a real application, it is desirable that the gas never reaches the dew point to avoid corrosion of the adsorber.

Zhang [80] assumed that in a standard bus (12.2 m long, 2.6 m wide, 3 m high, 49 seats) with a 207 kW diesel engine, cooling load around 17.6 kW, and a conventional air conditioner weighing about 300 kg, the waste heat that could be recovered from the exhaust gases would be at least 70 kW. The WCOP of 0.25 would be required to meet the cooling load demand and a SCP of about 200 Wkg^{-1} would be desirable to keep the bulk and cost of the equipment within the economic limits imposed by commercial applications. The system studied by this author could fit the demands of the WCOP but it was far from meeting the demand of the SCP. The low values of SCP were caused due to the low thermal conductivity of the bed (0.2 W m^{-1}K^{-1}) and the low wall heat transfer coefficient between the bed and the heat exchanger (25 Wm^{-2}K^{-1}). This system could probably be commercially applied if an adsorbent bed with enhanced heat transfer were used.

Lu *et al.* [85] developed an air conditioner with the pair zeolite-water that could be powered by the exhaust gases of a locomotive. This system, which scheme is shown in Fig. 21, was based on a laboratory prototype developed by Jiangzhou *et al.* [86]. It was designed to refrigerate the driver's cabin of a locomotive that ran in the Zhejiang province, East China.

The cooling power of such a system under typical running conditions ranged from 3 to 5 kW, with a COP of 0.21. The temperature inside the cabin was between 4 and 6 °C lower than the ambient temperature, while this same cabin, without refrigeration usually had a temperature of 2 to 5 °C higher than the ambient temperature.

The Fig. 22 shows the cooling power, and the inlet and outlet temperatures of the chilled water in the fan coil unit during a typical run of a locomotive from Hangzhou to Shanghai, when the average speed was between 100 and 120 km hr^{-1}. This system had a problem similar to that in the system studied by

Zhang [80], with respect to the cooling of the adsorbent in the adsorption phase. In the experiments with this machine, the temperature of the adsorbent bed at the end of the adsorption phase was close to 90 °C, which greatly reduced the cooling performance.
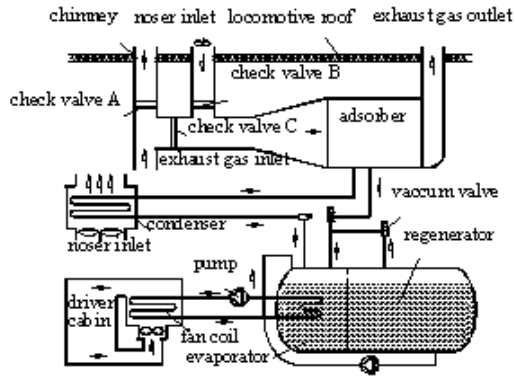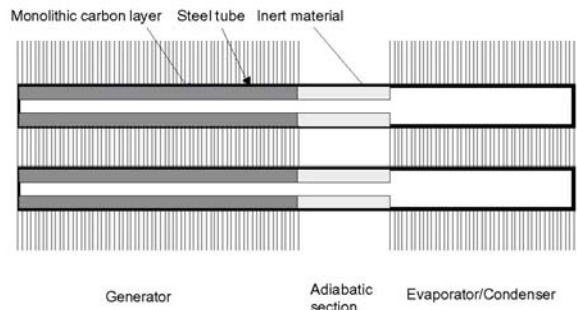

Fig. 21. Scheme of the adsorption air conditioner installed in the locomotive [85].

The authors remarked that the velocity of the locomotive and the rotating speed of the engine have significant influence on the cooling and heating power, respectively, of the air conditioner. This system is feasible and practical to be applied in a locomotive except when it pulls passenger cars, because in this condition, the train runs slowly and stops at every railway station. The cost of such a system is expected to be about US$5,000.
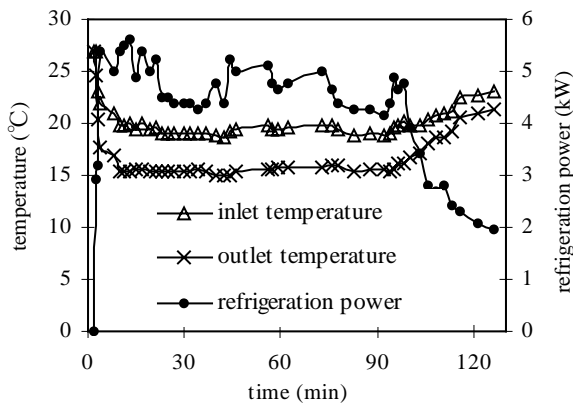
Fig. 22. Variation of chilled water temperature and refrigeration power from Hangzhou to Shanghai [85].

Tamainot-Telto and Critoph [87] studied a modular adsorption air conditioner, which was powered by hot air. The authors tested three different module configurations. The module that presented the best performance had 125 μm fins around the evaporator/condenser and around the adsorber, as shown in Fig. 23. The results of the experiments with this module showed that under typical conditions (generation temperature of 100 °C, condensing temperature of 30 °C and evaporation temperature of 15 °C), the cooling power was about 100 W, the SCP was about 600 Wkg⁻¹, and the COP was 0.20 without any heat regenerative process, or estimated to be 0.5 with a two bed regenerative cycle.


Fig. 23. Scheme of the modular adsorption air conditioner [87].

6. COMMERCIALLY PRODUCED ADSORPTION CHILLERS AND ADSORPTION SYSTEMS IN CCHPS

The adsorption refrigerators appeared on the market in 1986 and they were produced by the Nishiyodo Kuchouki, Co. Ltd.. The silica gel-water adsorption chillers produced by this company are sold in the American market by the HIJC USA Inc. This company estimated the payback of this chiller to about 2 to 3 years [88]. The chiller is driven by hot water from 50 to 90 °C, and the temperature of chilled water is close to 3 °C. The COP can reach 0.7 when the chiller is powered by hot water at 90 °C.

Another company producing silica gel-water adsorption chillers is Qianchuan Co. in Canada. The chillers from this company can be powered by hot water at 75 °C and yield chilled water at 14 °C with a reported COP of 0.6.

An adsorption chiller patented by Xia *et al.* [72] is currently working in the Shanghai Research Institute of Building Science as part of a solar powered air conditioner, and it is also used at a grain depot in Jiangsu Province, China, for cooling grain during hot summers. This adsorption chiller has been commercially produced on a small scale, and there are eight units in operation with a rated cooling power of 10 kW. The manufacturer (Jiangsu Shuangliang Air Conditioner Equipments Co.) has agreed to collaborate with the research team of the author to extend the series to 5 kW, 20 kW, 50 kW, 100 kW, and 200 kW units. A scheme and a photo of this chiller are shown in Fig. 24.
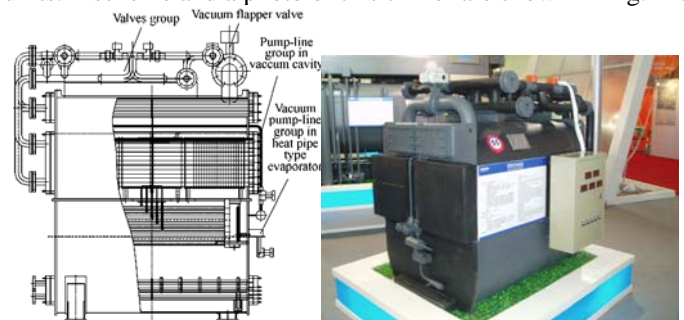
Fig. 24. Adsorption chiller developed in the Shanghai Jiao Tong University.

The small power adsorption chillers (10-200 kW) can be suitable for combined cooling, heating and power systems (CCHP) as demonstrated by a real application in the Malteser Hospital St. Johannes, in Germany, and by an experimental investigation performed by the research group of the author, in the Shanghai Jiao Tong University (SJTU).

The distributed energy utilization systems, like CCHP and CHP ones, with extensive employment of natural gas, seems to be the main direction of the Chinese policy for energy exploitation. Such systems can also increase the reliability of the power supply, which is vital to companies that work with computing, manufacturing and research functions. Furthermore, emissions of CO_2 and other air pollutants like NO_X, SO_2 and VOC compounds could also be substantially reduced. According to the US Department of Energy, CHP systems have the potential of reducing annual greenhouse gas emissions by at least 25 million tonnes of carbon if the US Government goal to double the total capacity of installed units by 2010 was met [89].

The CCHP system installed at the beginning of 2000, in the St. Johannes hospital is composed by a fuel cell, solar collectors, a heat storage vessel, a mechanical compression chiller, an adsorption chiller, an ice storage tank and cooling ceilings. The energy collected by 116 m^2 of solar panels and the waste heat from the fuel cell are stored as hot water in a vessel. The hot water drives a 105 kW Mycom ADR 30 adsorption chiller, manufactured by the Japanese company Mayekawa. The mechanical compression chiller is used to regulate the total cooling power of the system, but it is never in use during the peak hours, due to the presence of the ice storage tank [90].

The NG or LPG-fired micro-CCHP system studied in the SJTU is shown in Fig. 25. It is composed of a small-scale power generator set driven by a gas engine and a silica gel-water adsorption chiller. The refrigeration COP of this chiller is over 0.4 if it is driven by hot water at 85 °C. The overall thermal and electrical efficiency of the system is above 70%. This system could have a payback period between 2 and 3.2 years, for commercial buildings or between 1.7 and 2.4 years for hotels, if the natural gas price ranged from US$ 0.19 to 0.23 per Nm^3. Detailed information about this system is shown by Wang *et al.* [91].

Desiccant systems can also be integrated into a CCHP system, as studied by Maranthan [92]. This author optimized the operation conditions of a CCHP system in Maryland University, where the exhaust air stream from a 60 kW micro turbine was used to power an absorption system and regenerate a solid desiccant wheel. The system could provide 5,000 m^3h^{-1} of dehumidified air for space conditioning.

7. HEAT PIPES IN ADSORPTION SYSTEMS

The high initial costs of the machines and the low heat transfer properties of the adsorbers are among the limitations for the commercial application of adsorption systems. The use of heat pipes could help in the reduction of these problems, not only due to the high heat flux density provided by these devices, but also due to the lack of moving parts to drive the heat transfer medium, which makes the whole system cheaper and more reliable.

The condensation of the working fluid of the heat pipe can release the necessary heat to regenerate the adsorber while its vaporization can absorb the sensible heat and the sorption heat during the adsorption phase.

Meunier [93] mentioned a study carried out at LIMSI where extremely high heat transfer coefficients of about 10 kWm^{-2} were obtained with the utilization of heat pipes in adsorption systems.

Critoph [94] applied a heat pipe to heat and to cool the adsorber of an adsorption system. The author concluded that different fluids should be used for cooling and heating purposes. Fluids with different physical properties would avoid sub-atmospheric and very high working pressure, which is desirable because it eliminates both the occurrence of possible inward air leaks and the utilization of thick material to enclose the working fluid.

Vasiliev *et al.* [95] designed an adsorption system that could be powered by solar energy or electricity. Heat pipes were used in the heat transfer fluid and refrigerant circuits.

The heat sources supplied the necessary energy to evaporate the working fluid inside one of the heat pipe evaporators (16 in Fig. 26). When this fluid condensed, it released heat to regenerate the adsorbents (2). The two phase heat transfer device of this system was constructed as a vapour dynamic thermosyphon, which had one small boiler evaporator (16), two elongated cylindrical condensers inside the adsorber (9), a vapour chamber (16) with two flexible pipes for liquid flow (11), and one pipe for vapour flow (13). There were also two valves (10) on the pipes for liquid flow that were used to regulate the feeding of water into the boiler.
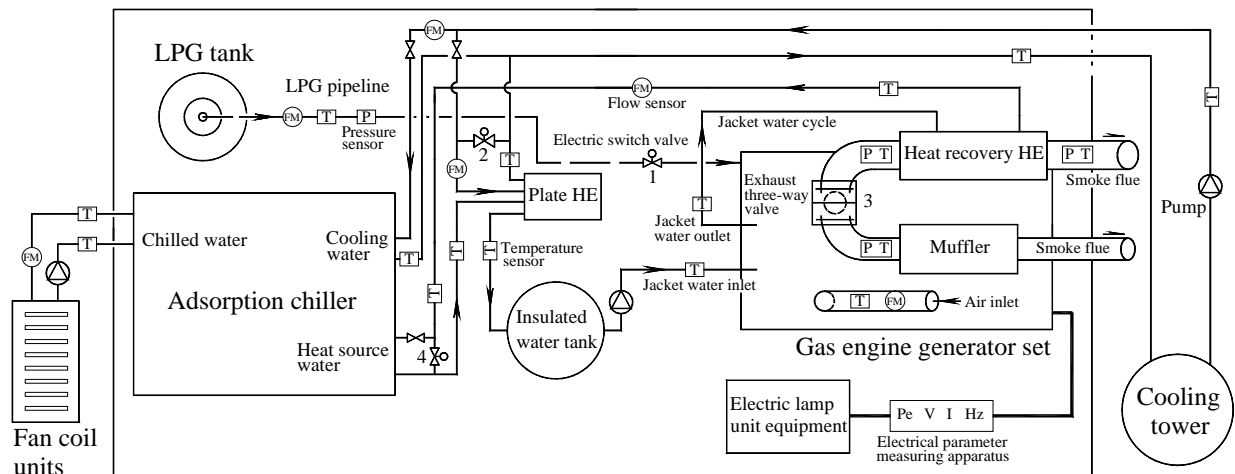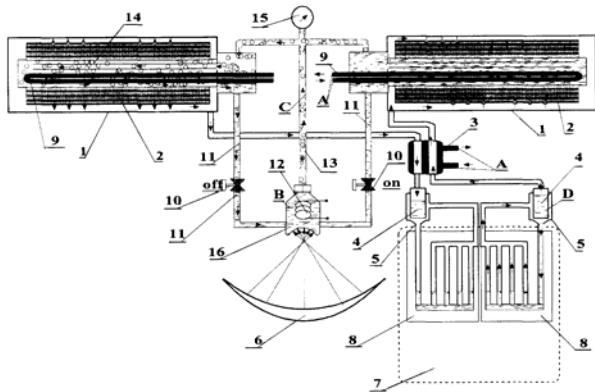

Fig. 25. Experimental CCHP layout: (T) temperature sensor; (P) pressure sensor; (FM) flow sensor; (Pe) electric power; (V) voltage; (I) current; (Hz) frequency [91].

Fig. 26. Scheme of the sorption refrigerator. 1) adsorbers; 2) sorption beds; 3) condenser; 4) porous evaporators; 5) condensers of the *spaghetti* heat pipes; 6) parabolic solar concentrator; 7) refrigerator box; 8) *spaghetti* heat pipes; 9) cylindrical condensers; 10) electrical valves; 11) flexible pipes for liquid flow; 12) electric heater; 13) pipe for vapour flow; 14) vapour channel; 15) pressure gauge; 16) boiler - evaporator. Circuits: A) heat sink; B) heat source (liquid); C) heat source (vapour); D) NH₃ [95].

A loop heat pipe was used to connect the refrigerant evaporator of the adsorption system (4 in Fig. 26) to the cold box. The condenser of the heat pipe (5) was placed on the outer surface of the refrigerant evaporator. The evaporation part of the multi-bent heat pipe was inserted along the walls of the refrigerator. These two heat pipes arcs were used as a second ammonia circuit, thermally connected with the first ammonia circuit (evaporators 4). When the temperature of the evaporators decreased and became lower than the temperature of the air inside the refrigerator, the ammonia inside the heat pipe evaporated to condensate on the outer surface of the evaporator. The heat transfer between the air inside the refrigerator and the cold heat pipe panel was performed by natural convection, and this panel could provide 300 W of cooling.

Besides the application of gravity heat pipes in the adsorption chillers powered by low temperature heat sources, recent research in the SJTU also employed heat pipes in the development of adsorption icemakers for fishing boats [96,97]. The introduction of this technology increased the heat transfer inside the adsorber and allowed direct use of exhaust gases as heat source and seawater as heat sink. Thus, the corrosion problems in the adsorber can be avoided.

In a recent work performed at this University, a split heat pipe adsorption icemaker, which employed compound adsorbent of $CaCl_2$ and activated carbon in the proportion 4:1, was designed and constructed. This system, which is presented in Fig. 27, contains two adsorbers, each one with 1.88 kg of $CaCl_2$, and can reach an evaporation temperature of –42 °C. At evaporating temperatures of –35, ‑25 and –15 °C, the cooling powers were 0.9, 1.2 and 1.4 kW, respectively, with a COP of 0.41 for the latter condition. The cooling power per kg of salt based only in the cooling period can be as high as 731 Wkg^{-1}. The heat transfer coefficients, for the heating and the cooling

phases obtained with this heat pipe, were similar and around 156 $Wm^{-2}K^{-1}$. Such a machine can operate with and without refrigerant mass recovery, but the mass recovery increased the SCP with 22 % and the COP with 24 %, when the evaporation temperature was –25 °C. Further details about the experimental set-up and system performance are soon to be published.
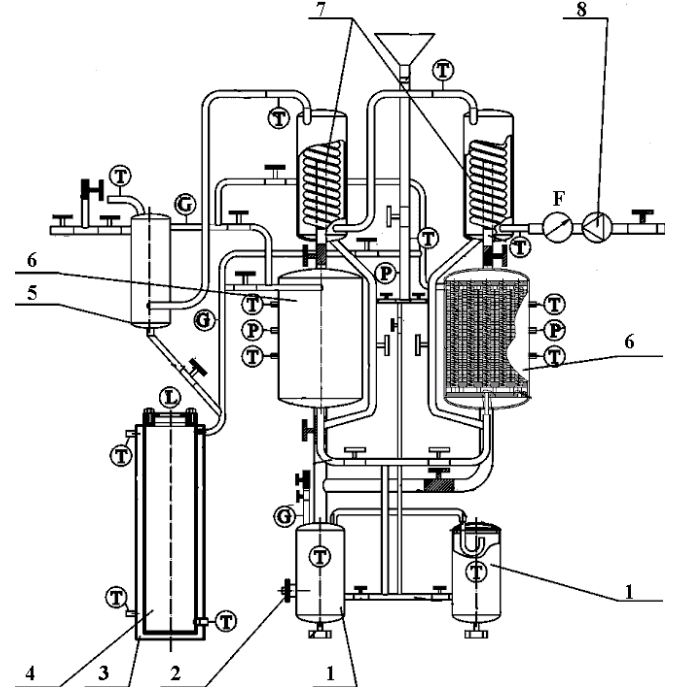
Fig. 27. Scheme of the adsorption system with split heat pipe. 1) boiler; 2) electric heater; 3) cooling jacket; 4) evaporator; 5) condenser; 6) adsorber; 7) coil pipe cooler; 8) water pump; (F) flow sensor; (G) pressure gauge; (L) level sensor; (P) pressure sensor; (T) temperatures sensor.

The silica gel-water chiller patented by Xia *et al.* [72] used a heat pipe structure on the evaporator not only to provide high heat transfer flux but also to increase the reliability of the system with reduction in the manufacturing costs. The evaporators utilized in the chiller are combined together by a heat-pipe heat exchanger (HPHE), as shown in Fig. 28.
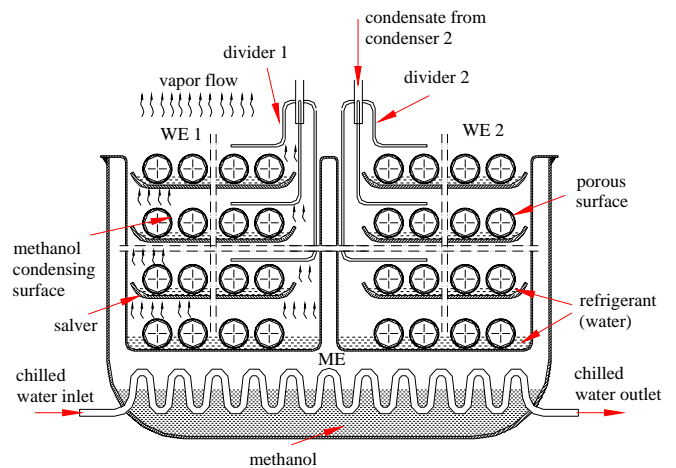
Fig. 28. Scheme of the heat pipe evaporator.

The design of the evaporator simplifies the construction of the system, as it substitute the two water evaporator/condenser found in other chillers, like that one studied by Liu *et al.* [71], by a single methanol evaporator.

The exterior surface of the copper tubes in the water evaporator (WE) is a porous medium that enhances the evaporation capability, so the volume of the evaporator could be reduced. The methanol evaporates on the exterior surface of the heat exchange tubes in the methanol evaporator (ME) of the HPHE and condenses on the internal surface of the tubes in one WE (for example, WE1). Simultaneously, the WE2 collects the condensate coming from the condenser through the divider. Under this situation, the temperature inside the WE2 is higher than the temperatures of the WE1 and the ME. Accordingly, the heat exchanges from the WE2 to the WE1 and to the ME are blocked by the working principle of the gravitational heat pipe.

For a typical working condition when the chiller is powered by hot water at 85 °C, a SCP higher than 100 Wkg^{-1} could be obtained, with a COP of 0.43. When powered by hot water at 60 °C, the SCP and COP will be a half of those obtained under the typical working condition. Other experimental results can be seen in Tab. 1.

Tab. 1. Experimental results of the silica gel-water adsorption chiller

| Hot water temp. [°C]	Cooling water temp. [°C]	Chilled water temp. [°C]		Cooling power [kW]	COP	SCP [W kg^{-1}]	Cycle time [s]
		Inlet	Outlet				
78.8	31.3	20.5	16	8.32	0.31	80	1680
81.8	31.3	20.7	16.3	9.33	0.34	89.7	1920
86.8	30.9	21.1	16.3	10.62	0.40	102.1	1920
59.7	30.4	20.5	18.2	4.80	0.39	46.2	
69.1	30.3	19.6	16.2	7.57	0.38	72.8	
84.4	30.5	21.5	16.5	10.88	0.43	104.6	
85.3	30.6	20.9	16.1	10.44	0.40	100.4	2280
80.3	30.2	15.8	12.1	8.26	0.38	79.4	
82.5	30.4	15.8	11.9	8.69	0.39	83.6	
83.8	30.8	15.4	11.8	8.6	0.38	82.7	

Another recent project in the SJTU employed a similar evaporator heat pipe device in a compact adsorption air conditioner (CAAC). The schema of this machine is shown in Fig. 29. This chiller was designed for combined utilization with a fuel cell for home use, and which could be considered as a mini CCHP system.

There are two vacuum chambers in the chiller, and each one encloses one adsorber (with 5 kg of silica gel), one condenser and one evaporator, as shown in Fig. 30. As these equipments are inside the same chamber, there is no need of vacuum valves among them.

When the adsorber is heated, the water is desorbed and vapour flows to the condenser. The condensed water is moved by gravity to the evaporator, which is located below the former device. During the adsorption phase, as the adsorber is cooled, its pressure decreases and water vapour from the evaporator flows back to the adsorbers.
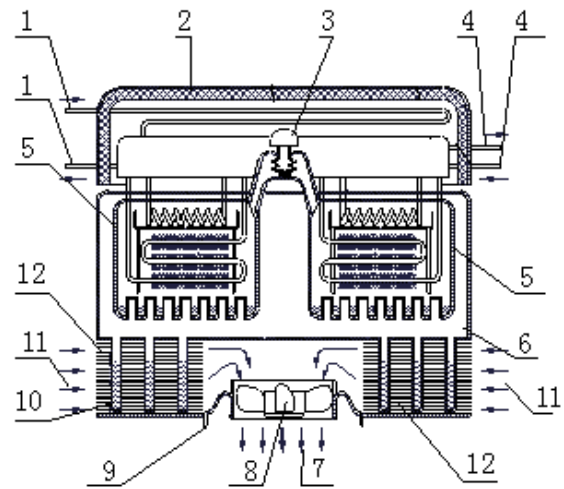
Fig. 29. Scheme of the air conditioner. 1) outlet and inlet of the adsorber cooling medium; 2) heat insulation; 3) mass transfer valve 4) outlet and inlet of the adsorber heating medium; 5) water vacuum chamber; 6) methanol vacuum chamber; 7) outlet air; 8) fan; 9) drain; 10) working fluid (methanol);11). inlet air; 12) methanol evaporator.
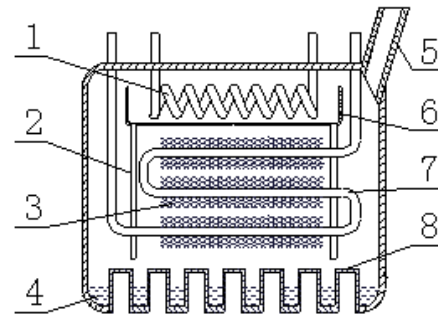
Fig. 30. Scheme of the water vacuum chamber of the air conditioner. 1) condenser; 2) water flow channel; 3) silica gel; 4) working fluid (water); 5) mass transfer pipe; 6) collector plate; 7) adsorber; 8) evaporator.

A methanol vacuum chamber, comprised by an evaporator and a condenser, surrounds the water vacuum chambers. The function of the methanol chamber is to transfer heat from the indoor air to the water evaporator. The methanol condenser and the water evaporator are integrated into a single part called "separator". When the indoor air flows through the methanol evaporator, the methanol evaporates and condenses on the surface of the water evaporator. The condensate returns to the methanol evaporator by gravity.

Evaluation tests were conducted under the working conditions shown in Tab. 2, and the COP and the cooling power are shown in Tab. 3. If some of the problems associated with the manufacturing process can be solved, this chiller is expected to reach a cooling power of 995 W with a COP of 0.48, when powered by hot water at 85 °C and cooled by cold water at 30 °C.

Tab. 2. Working conditions for the adsorption chiller.

Flow rate of hot water [L min^{-1}]	5
Flow rate of cooling water [L min^{-1}]	10
Flow rate of the air [m^3 min^{-1}]	4.5
Indoor air dry bulb temperature [^{o}C]	27
Indoor air wet bulb temperature [^{o}C]	19
Cycle time [min.]	38 or 36[*]
Heating time of each adsorber [min.]	15
Cooling time of each adsorber [min.]	15
Heat recovery time [s]	20
Mass transfer time [min.]	3 or 2[*]
Time for switching the valves [s]	80

[*] if the temperature of the inlet heating water is 90 °C.

Tab. 3. Cooling power and COP of the adsorption chiller.

Heating water inlet temp. [^{o}C]	Cooling water inlet temp.[^{o}C]			Cooling water inlet temp.[^{o}C]		
	28	30	32	28	30	32
	COP			Cooling Power [W]		
90	0.319	0.304	0.290	792.2	722.5	659.3
85	0.339	0.321	0.301	794.6	718.5	653.9
80	0.319	0.298	0.275	680.1	615.0	548.6
75	0.290	-	-	558.0	-	-
70	0.291	-	-	489.3	-	-

8. KEY ISSUES FOR THE DEVELOPMENT OF ADSORPTION SYSTEMS

The adsorption systems must have their size and cost reduced to become more commercially attractive. The most promising alternatives to achieve these goals include the enhancement of the internal and external heat transfer of the adsorber, to increase the SCP, and the improvement of the heat management, to increase the COP. The main technologies to enhance the external heat transfer in the adsorber are related to the increase of the heat exchange area, the use of coated adsorbers and the utilization of heat pipe technology, which was described in the previous section. To improve the internal heat transfer, the most suitable option is the employment of consolidated adsorbents.

8.1 Extended surfaces

Several types of extended surfaces can be considered, such as finned tubes, plate heat exchangers and plate-fin heat exchangers. This solution is suitable if the wall heat transfer coefficient is not low and if there is no swelling or shrinking effect of the sorbent which could produce a considerable alteration in this coefficient. The drawback of this technology is that it increases the thermal capacity of the adsorber; therefore, extended surfaces heat exchangers require efficient heat management to produce reasonable COPs. Furthermore, this solution should be avoided if the operation pressure is very low and the Knudsen effect can occur [93].

8.2 Coated adsorbers

The utilization of coated adsorbers is particularly suited for applications where high COP is not as important as high SCP. This technology consists in the increase of the wall heat transfer coefficient by the effective decrease of the contact

thermal resistance between the heat exchange surface and the adsorbent. Dunne [98] developed coated tubes where zeolite crystals monolayers grew on the tube metal surfaces. The heating rate of this adsorber is higher than 1500 W per kg of sorbent. Bou et al. [99] developed a coated heat exchanger where the adsorbent bed was inserted in an expanded graphite plate. With this technique, the contact between the heat transfer fluid and the adsorbent is not as close as in the previous coated tube, but the ratio between the mass of adsorbent and the mass of inert material is much higher, since the thickness of the adsorbent bed can reach a few millimetres.

The main disadvantage of using coated adsorber is the very high ratio between the inert mass and the adsorbent mass, which spoils the COP. In order to overcome this drawback, a very effective heat management is required. Restuccia and Cacciola [30] compared by simulation the performances of two heat pumps in which one of them had an adsorber with coated surface and in the other one, the adsorber was filled with pelleted zeolite. The coated surface adsorber had a thin layer (1mm) of zeolite, which was synthesized outside the tubes of a tube and shell heat exchanger. The system with pelleted zeolite was from a previous study performed by van Benthem et al. [24].

The system with coated tube had a cooling power about 3.6 times higher than that obtained with the system that employed pelleted zeolite. Due to the utilization of heat recovery process in both systems, and the COP of the former was only 2 % lower than the COP of the later.

8.3 Consolidated and composite adsorbents

Consolidated adsorbent with high thermal conductivity can be considered as the most promising alternative to enhance the heat transfer within the adsorber. Poyelle et al. [31] used a consolidated composite compound made from zeolite and expanded graphite with enhanced heat transfer properties in their experiments and achieved a SCP four times higher than that obtained using zeolite pellets.

Guilleminot et al. [6] studied a consolidated composite compound made from a mixture of zeolite and metallic foam. The compound produced from zeolite and copper foam had a thermal conductivity of 8.0 Wm^{-1}K^{-1}, which was 22 times higher than that of consolidated zeolite. The authors stressed the importance of the metallic foam material used in the compound, as the thermal conductivity obtained with the compound manufactured from zeolite and nickel foam was only 1.7 Wm^{-1}K^{-1}.

Tamainot-Telto and Critoph [83] studied the performance of a consolidated compound of activated carbon and organic binder in an adsorption system for ice making. They concluded that the system with the consolidated compound had a SCP 90 % higher than that of the system with granular carbon.

Wang et al. [17] developed a consolidated compound, which is shown in Fig. 31, made from a mixture of $CaCl_2$ and activated carbon. Experiments performed by these authors showed that the utilization of this compound could lead to a cooling density 35 % higher than that obtained by the use of powder $CaCl_2$.

In recent work, Wang et al. [18] studied a consolidated compound, made from $CaCl_2$ and expanded graphite. This compound presented a thermal conductivity of more than 32 times higher than that of powder $CaCl_2$. An adsorption system

using this compound could have a cooling density of about 330 MJm^{-3} at –10 °C, which is about 45 % higher than that obtained with powder $CaCl_2$. Fig. 32 shows the consolidated compound before and after the adsorption.

Fig. 31. Consolidated composite adsorbent made from $CaCl_2$ and activated carbon.
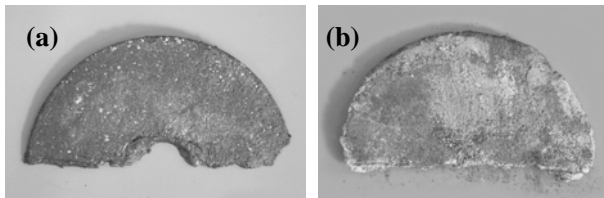
Fig. 32. Consolidated composite adsorbent from $CaCl_2$ and expand graphite. (a) Before adsorption, (b) after adsorption [18].

Eun *et al.* [11], studied the thermal and mass transfer properties of a compound made from silica gel and expanded graphite. Composite blocks with 20 to 30 % of graphite mass, and under a compression pressure between 4 and 40 MPa, showed a permeability of between 3 and 40×10^{-12} m^2, and a thermal conductivity of between 10 and 20 $Wm^{-1}K^{-1}$. These values of thermal conductivity are much higher than the 0.17 $Wm^{-1}K^{-1}$ usually found in granular silica gel packed bed.

Non-uniform reaction blocks, made from metallic salts impregnated into an expanded graphite matrix, were manufactured by Lee *et al.* [19]. These blocks were designed to improve the heat and mass transfer performance of chemical heat pump adsorbers. In contrast with other compounds that have uniform properties, such as the bulk density and the expanded graphite mass fraction, the studied blocks were prepared to increase the bulk density gradually in the radius direction from 165 to 394 kg m^{-3}. The experimental results showed that these blocks have much better heat transfer capability, since the temperature gap between the inner and outer sides of the bed was smaller than that in the uniform reaction blocks.

Han *et al.* [12] measured the effective thermal conductivity and the gas permeability of a compound adsorbent made from expanded graphite impregnated with $MnCl_2$. The compound tested had a graphite bulk density of between 100 and 250 kg m^{-3}, and the values obtained were in the range from 14.0 to 25.6 $Wm^{-1}K^{-1}$ for the thermal conductivity and between 8.1×10^{-15} and 2.5×10^{-13} m^2 for the permeability. The results of a simulation using these experimental data showed that when the operating pressure was equal or bellow 1.0 bar and the graphite bulk density of the reactive medium was higher than 200 kg m^{-3}, the rate of global conversion was significantly reduced by the mass-transfer limitation. The absence of a distinctive heat front in the adsorbent was noticed, which could mean that heat transfer is not a limiting factor in the performance of the studied compound.

In general, consolidated adsorbents have lower mass-transfer properties than granular adsorbents, which could lead to very low adsorption rates especially for refrigerants evaporating under atmospheric pressure, such as water or methanol. Thus, besides experiments to identify the thermal conductivity and the wall heat transfer coefficient of these compounds, experiments to identify their permeability must also be performed when a new consolidated adsorbent is formulated.

By controlling the compression pressure, and the mass ratio between the adsorbent and the inert material, it is possible to control the density of the final compound and its properties of heat and mass transfer.

8.4 Advanced cycles

The aim of the researches focused on advanced cycles with heat management is the increase of the COP, since in the conventional adsorption cycle, this figure of merit is usually smaller than 0.4 [100].

In the cycle with heat recovery, one adsorber, at the beginning of the adsorption phase, releases heat to a cold adsorber, which is starting the generation phase. Theoretically, this process can continue until the temperatures of both adsorbers are similar, but for practical reasons, it usually stops when the difference between the temperatures is within the range of 5 to 15 °C. Then, the adsorbers are connected to a heat sink and heat source, to finish, respectively, the adsorption and the generation process. Due to this heat management, about 35% of the total energy transmitted to each adsorber can be internally recovered, including part of the sorption enthalpy [44].

Higher COPs can be expected with cycles that employ heat regeneration process, which is also called thermal wave. The inlet fluid temperatures (points A and C in Fig. 33) are the same as the heat sink and heat source temperatures, respectively. The outlet fluid temperatures (points B and D) change with the time.
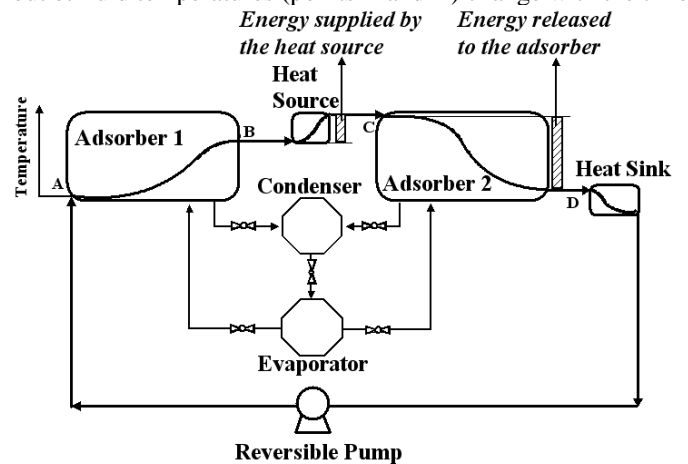
Fig. 33. Adsorption cycle with heat regeneration.

In the heat regeneration process, the heat transfer fluid flows successively through: i) one adsorber, which is being cooled; ii) the heat source; iii) another adsorber, which is being heated; and iv) the heat sink. When the gradient of temperature between the inlet and outlet heat transfer fluid from the first adsorber is large, only a limited heat power is required from the

heat source in order to provide a large heat power to the second adsorber. According to Pons and Poyelle [44], this is possible because the large amount of energy recovered from the first adsorber is regenerated (according to the thermodynamics second law) by the energy supplied at high temperature. The heat regeneration can be a very efficient heat storage process because about 65% of the total energy received by each adsorber can be internally recovered [44]. Furthermore, the heat transfer fluid circuit can be very simple. It needs only a reversible pump and valves are not necessary.

Tchernev and Emerson [101] developed a double bed zeolite-water adsorption air conditioner that employed the heat regeneration process to increase the COP and obtained experimental values between 1.6 and 1.0, according to the ambient temperature that ranged from 27 to 38 °C. The SCP was not sensitive to the ambient temperature and it was 36 W kg^{-1}. In the heat regenerative cycle, the flow rate and the type of heat transfer fluid have great influence on the performance of the adsorption system. High flow rates increase the SCP but decrease the COP [38], thus this variable must be chosen carefully to ensure that the machine will have the expected performance. The machine developed by Tchernev and Emerson [101] could achieve a SCP of 108 W kg^{-1}, but in this case, when the ambient temperature was 27 °C, the COP was reduced to 0.7.

In the heat regenerative system developed by Miles and Shelton [102], the working pair used was activated carbon-ammonia, and the COP obtained varied between 1.19 and 0.42, for ambient temperatures from 20 °C to 35 °C.

Another kind of heat regenerative cycle was suggested by Critoph [40], in which the refrigerant serves as heat transfer medium. A thermodynamic model presented by the author predicted a COP of 0.95 with an evaporation temperature of 0 °C and a condensation temperature of 42 °C.

Wade et al. [34] simulated a regenerative adsorption cycle with eight beds that could recover 76 % of the waste energy from the adsorption process. During this cycle, the hot thermal fluid that left the hot adsorber (Adsorber **1** in Fig. 34) pre-heated the adsorbers **2** to **4**, before be completely cooled by the heat sink. The cold heat transfer fluid flowed from the heat sink towards the adsorber at the adsorption phase (Adsorber **5**). After remove the heat from the adsorber **5**, the heat transfer fluid continued its path to pre-cool the adsorbers **6** to **8,** and be pre-heated. Then, the thermal fluid was heated until the generation temperature by an external heat source before enters the adsorber **1**. This fluid route was maintained during a specific period, before the adsorbers switch position.
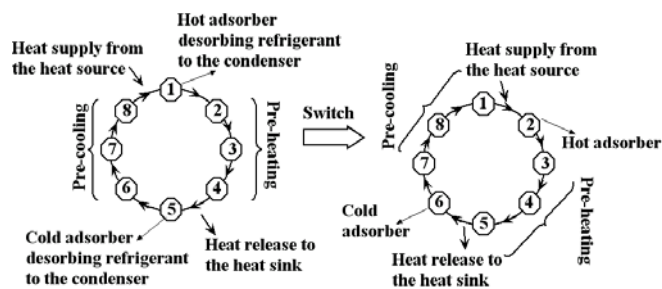
Fig. 34. The design of heating/cooling thermal fluid loop with eight adsorbers.

The previous work was the base for the design of a prototype with four beds that was used to produce cooling at -136 °C [103]. The energy input necessary to produce 1 W of cooling in this prototype was 76.6 W, which was much lower than the 165 W required in the system without heat regeneration.

Neveu and Castaing [36] proposed a heat recovery cycle between two adsorbers filled with different metallic salts. The adsorption chemical reaction inside the first adsorber releases the necessary heat to regenerate the salt placed in the second adsorber. Thus, only the salt in the first adsorber needs external heat supply. The use of $MnCl_2$ in the first adsorber and $NiCl_2$ in the second adsorber could produce a theoretical COP of 0.6 at evaporation temperature of –10 °C, while at this same evaporation temperature, the utilization of $SrCl_2$ and $FeCl_2$ would produce a COP of 0.7. In both cases, the assumed condensation temperature was 40 °C, and ammonia was the refrigerant desorbed and adsorber.

A different approach to improve the COP of sorption systems was followed by Satzger et al. [39]. The authors presented the theoretical results that can be expected when absorption and chemical reaction chillers operated together under triple and quadruple effect. The absorption chiller is used in the bottom stage due to temperature restrictions observed in this kind of machine, and the chemical reaction chiller is employed in the topping stage. A system performing the cycle with triple effect in double stage only shows higher COP than a double stage absorption system if the COP of the topping machine is higher than 0.3. When the system operates under the three stages quadruple effect cycle, the theoretical COP can be close to 2.0 if the COP of the chemical sorption chiller is 0.5 or about 1.6 with the COP of the later is 0.3. In both cases, the COP would be higher than the value of 1.2, which was assumed for a double stage absorption chiller.

Besides the utilization of heat management cycles, it is possible to employ refrigerant mass recovery between two adsorbent beds to enhance effectively both the cooling power and the COP of adsorption systems. Szarzynski et al. [40], analyzed cycles with refrigerant vapour recovery and concluded that the SCP could be increased by about 20 %. This author did not notice major changes in the COP. Wang [48] compared the COP of adsorptions systems with and without vapour recovery and found that the former could produce a COP from 10 to 100 % higher than the latter. The difference between the COPs was higher at lower generation temperatures.

In the experiments carried out by Oliveira et al. [51], the operation of an icemaker with mass recovery enhanced the adsorbed mass with about 37 to 42 % when compared to the operation of the system without this process. The pair employed in the experiments was activated carbon-ammonia, and the generation temperatures were 85 and 115 °C. At the lowest generation temperature, the utilization of the cycle with mass recovery in double stage produced the best results, while at the highest generation temperature, the best results were obtained when the conventional mass recovery was employed. The cycle with mass recovery in double stage studied by these authors inserts the process of mass recovery at the end of the generation/adsorption phase of the conventional double stage cycle to increase the amount of adsorbed mass from the evaporator.

The adsorption research team of the SJTU has successfully used mass recovery in the development of adsorption systems. The improvements were in the order of 7 to 22 % for the SCP and 20 to 30 % for the COP, depending on the application and operation conditions [71,81].

Although the advanced cycles can increase the performance of the adsorption systems, the complexity of the system also increases. Therefore, among the studied advanced cycles, the mass recovery cycle seems to be one of the most cost effective ways to improve both COP and SCP.

9. CONCLUSIONS

Since the interest in adsorption systems was renewed in the last 20 years, the COP and the SCP of these systems greatly increased due to the work of several research groups. The Tab. 4 shows some of the best performances obtained by different prototypes manufactured during this period, for the applications and heat sources discussed in this paper. The results should not be compared to one another, as they were obtained under different working conditions, but they should be used as a reference of what can be expected from these systems.

Most solar icemaker prototypes have a daily ice production between 4 and 7 kg per m^2 of solar collector, with a solar COP between 0.10 and 0.15. These values could increase even more if the future machines start to be manufactured with consolidated adsorbent.

Solar energy can also drive desiccant systems that can be are used to remove the latent load and humidity of the air. Simple systems as described by Ismail [75] and Toruwa [76] can be applied for air conditioning in grain storage. These systems can also be combined with evaporative cooling or with mechanical compression systems to increase their performance. In both cases, the desiccant material can be regenerated by waste heat or solar energy. Such applications are already found in some buildings in Europe [79].

After several projects aimed to increase the performance of the adsorption chillers with the pair silica gel-water, these chillers can be currently found on the market and they are already under operation as part of the air conditioning systems located in buildings or in a chinese grain depot.

As the adsorptive beds of the chillers can be regenerated by low-grade temperatures, waste heat or solar energy can be used as heat source. These chillers can also be employed in CCHP systems as demonstrated by the application in a hospital situated in Germany, and by recent studies in the Shanghai Jiao Tong University. The overall thermal and electrical efficiency in these systems can be above 70%. When applied to commercial buildings, a CCHP with rated electricity power of 12 kW, rated cooling power of 10 kW and rated heating power of 28 kW would have a payback period of between 2 and 3.2 years if the price of the natural gas ranged from US$ 0.19 to 0.23 per Nm^3 [91].

Tab. 4. Performance of adsorption systems for different applications.

Application	Heat source temperature or insolation	Working Pair	COP	SCP or ice production	Year	Ref.
Ice making	20 MJm^{-2}day^{-1}	AC-Methanol	0.12	6 kg day^{-1} m^{-2}	1986	54
Ice making	105 °C	AC- NH$_3$	0.10	35 W kg^{-1}	1997	83
Ice making	18.1 – 19.2 MJm^{-2}day^{-1}	AC-Methanol	0.12 - 0.14	5.0 – 6.0 kg day^{-1} m^{-2}	2002	57
Ice making	17 – 20 MJm^{-2}day^{-1}	AC-Methanol	0.13 - 0.15	6.0 – 7.0 kg day^{-1} m^{-2}	2004	58
Ice making	15.4 MJm^{-2}day^{-1}	Silica gel-water	[1]0.16	2.05 MJ day^{-1} m^{-2}	2004	63
Ice making	20 MJm^{-2}day^{-1}	AC+blackened steel-Methanol	0.16	[2]9.4 kg day^{-1} m^{-2}	2004	64
Ice making	<120 °C	AC-Methanol	0.18	27 W kg^{-1}	2005	82
Ice making	<120 °C	AC+CaCl$_2$-NH$_3$	0.41	[3]731 W kg^{-1}	2005	3
Chilled water	55 °C	Silica gel-Water	0.36	3.2 kW Unit^{-1}	2001	69
Chilled water	100 °C	AC-Methanol	0.4	73.1 W kg^{-1}	2001	70
Chilled water	65 °C	Silica gel-Water	0.28	12.0 kW Unit^{-1}	2003	72
Chilled water	75 – 95 °C	Silica gel-Water	0.35-0.60	15.0 kWm^{-3}	2004	73
Chilled water	80 – 95 °C	Silica gel-Water	0.3-0.6	[5]20 Wkg^{-1}	2004	74
Chilled water	80 °C	Silica gel-Water	0.33-0.5	91.7-171.8 W kg^{-1}	2005	71
Air conditioning	232 °C	AC-NH$_3$	0.42-1.19	[6]NA	1996	102
Air conditioning	204 °C	Zeolite-Water	0.6-1.6	36-144 W kg^{-1}	1988	101
Air conditioning	230 °C	Zeolite-Water	0.41	97 W kg^{-1}	1999	31
Air conditioning	310 °C	Zeolite-Water	0.38	25.7 W kg^{-1}	2000	80
Air conditioning	100 °C	AC-NH$_3$	0.2	600 W kg^{-1}	2003	87
Air conditioning	230 – 300 °C	Zeolite-Water	0.20 - 0.21	21.4 – 30 W kg^{-1}	2004	85

[1] Average value obtained during 30 days of continuous operation.

[2]. Based on the area of the adsorber, which was different from the area of the reflector panels.

[3]. The SCP is based on the mass of CaCl$_2$ inside one adsorbent bed and on the adsorption time.

[4] To be published in International Journal of Refrigeration.

[5] At generation temperature of 95 °C.

[6] Not informed.

Unless higher generation temperatures are employed to regenerate the beds of the chillers, which is not always possible for solar powered systems, further improvements in the COP may be obtained only with new designs that reduce the thermal capacity of the adsorber, because at low generation temperatures, just a limited heat recovery is possible.

When higher heat source temperatures are available, which is the case of CCHP systems, it is reasonable to expect that COPs higher than 2 could be obtained with chemical reaction chillers using internal heat management, as the predicted Carnot COP at 300 °C can be as high as 3 [93].

The cost of adsorption chillers, that nowadays is about US$ 7,000 for a 10 kW-unit, could be reduced by mass production and by the use of technologies that could reduce or simplify their components. Heat pipes are among the technologies suitable to accomplish such a goal, as demonstrated with some experiments performed at the SJTU [72, 96,97].

Consolidated compound adsorbents have shown their potential to increase the cooling performance of the adsorption refrigeration machines and should be employed when ever possible. A modular air conditioner with consolidated carbon presented a SCP of 600 Wkg^{-1} and a COP of 0.2 [87]. This prototype was produced in a double module configuration with small cooling power (100 W). Experiments with higher number of modules have not been tested yet to confirm if this high SCP could be kept under higher cooling power applications.

The adsorption research team of the SJTU recently achieved successful results with the utilization of consolidated composite compound. A new prototype of adsorption icemaker presented a cooling power, based on the length of the cooling period and in the mass of salt, of 731 Wkg^{-1}, and a COP of 0.41, when the evaporation temperature was −15 °C. This prototype was designed to operate on fishing boats and uses split heat pipe technology to allow direct heating and cooling of the adsorbers by exhaust gases of diesel engines and by seawater, respectively.

From the examples presented, it is possible to consider that adsorption systems can be an alternative to reduce the CO_2 emissions and the electricity demand when they are driven by waste heat or solar energy. Although, for a broader utilization, the researches should continue aiming for improvements in heat transfer, reductions of manufacturing costs, and for the formulation of new adsorbent compounds with enhanced adsorption capacity and improved heat and mass transfer properties.

ACKNOWLEDGEMENTS

REFERENCES

[1] R. E. Critoph (1988) Performance limitations of adsorption cycles for solar cooling. Solar Energy. 41(1); 21-31.

[2] L. Luo, M. Feidt. (1992) Thermodynamics of adsorption Cycles: A Theoretical Study. Heat Transfer Engng. 13(4); 19-31.

[3] Y. Teng, R. Z. Wang, J. Y. Wu (1997) Study of the Fundamentals of Adsorption Systems. Appl. Thermal Engng. 17(4); 327-338.

[4] U. Huber, F. Stoeckli, J. P. Houriet (1978) A generalization of the Dubinin-Radushkevich equation for the filing of heterogeneous micropore systems in strongly activated carbons. J. Colloid and Interface Science. 67(2); 195-203.

[5] F. P. Passos (1986) Etude des couples charbon actif/methanol et de leur application a la refrigerations solaire. Ph.D. Thesis. Dep Mecanique, Ecole Polytechnique Federale de Lausanne; Switzerland; 101 p.

[6] J. J. Guilleminot, A. Choisier, J. B. Chalfen, S. Nicolas, J. L. Reymoney (1993) Heat transfer intensification in fixed bed adsorbers. Heat Recovery systems & CHP. 13(4); 297-300.

[7] S. Mauran, P. Prades, F. L`Haridon (1993): Heat and mass transfer in consolidated reacting beds for thermochemical systems. Heat Recovery Systems & CHP. 13(4); 315-319.

[8] R. E. Critoph (1996) Evaluation of alternative refrigerant-adsorbent pairs for refrigeration cycles. Appl. Thermal Engng. 16(11); 891-900.

[9] Z. Liu, Y. Lu, J. Zhao (1998) Zeolite-active carbon compound adsorbent and its use in adsorption solar cooling tube Solar Energy Materials and Solar Cells. 52; 45-53.

[10] J. J. Guilleminot, (1998) From pellet to composite adsorbent bed: evolutions of adsorber technologies. Proc. of Fundamentals of Adsorption (FOA6). France.

[11] T. H. Eun, H. K. Song, J. H. Han, K. H. Lee, J. N. Kim (2000) Enhancement of heat and mass transfer in silica-expanded graphite composite blocks for adsorption heat pumps: Part I. Characterization of the composite blocks. Int. J. Refrig. 23; 64-73.

[12] J. H. Han, K. H. Lee, D. H. Kim, H. Kim (2000) Transformation analysis of thermochemical reactor based on thermophysical properties of graphite-$MnCl_2$ complex. Ind. Eng. Chem. Res. 39; 4127-4139.

[13] R. G. Oliveira, Z. Tamainot-Telto, V. Silveira Jr (2001) Equilibrium characterisation of carbon C119-ammonia and carbon C119-dimethyl ether pairs and application in adsorption refrigeration design. Proc. of XVI Brazilian Congress of Mechanical Engineering (COBEM 2001). Brazil.

[14] Z. Tamainot-Telto, R. E. Critoph (2001) Monolithic carbon for sorption refrigeration and heat pump applications. Appl. Thermal Engng. 21; 37-52.

[15] A. Freni, M. M. Tokarev, G. Restuccia, A. G. Okunev, Yu. I. Aristov (2002) Thermal conductivity of selective water sorbents under the working conditions of a sorption chiller. App. Thermal Engng. 22; 1631-1642.

[16] M. Li, H. B. Huang, R. Z. Wang, L. L. Wang, W. D. Cai, W. M. Yang (2004) Experimental study on adsorbent of activated carbon with refrigerant of methanol and ethanol for solar ice maker. Renewable Energy. 29; 2235-2244.

[17] L. W. Wang, R. Z. Wang, J. Y. Wu, K. Wang (2004) Compound adsorbent for adsorption ice maker on fishing

boats. Int. J. Refrig. 27; 401-408.

[18] K. Wang, R. Z. Wang, L. W. Wang, (2005) Composite adsorbent of $CaCl_2$ and expanded graphite for adsorption ice maker on fishing boats. Submitted to Int. J. Refrig.

[19] C. H. Lee, S. H. Park, S. H. Choi, Y. S. Kim, S. H. Kim (2005) Characteristics of non-uniform reaction blocks for chemical heat pump. Chem. Engng Science. 60; 1401-1409.

[20] J. J. Guilleminot, F. Meunier, J. Paklesa (1987) Heat and mass transfer in a non-isothermal fixed bed solid adsorbent reactor: A uniform pressure-non-uniform temperature case. Int. J. Heat Mass Transfer. 30(8); 1595-1606.

[21] S. H. Cho, J. N. Kim (1992) Modeling of a silica gel/water adsorption-cooling system. Energy. 17(9); 829-839.

[22] H. D. Hermes, J. A. Pares, E. Velo, L. Puigjaner (1995) Modelling and sizing of gas-solid chilling machines. Computers Chem. Engng. 19 (Suppl.); S333-S338.

[23] L. M. Sun, A. N. Ben, F. Meunier (1995) Numerical study on coupled heat and mass transfers in an adsorber with external fluid heating. Heat Recovery Systems & CHP. 15(1); 19-29.

[24] G. H. W. van Benthem, G. Cacciola, G. Restuccia (1995) Regenerative adsorption heat pumps: optimization of the design. Heat Recovery System & CHP. 15(6); 531-544.

[25] E. J. Hu (1996) Simulated results of a non-valve, daily-cycled, solar-powered carbon/methanol refrigerator with a tubular solar collector. Appl. Thermal Engng. 16(5); 439-445.

[26] H. B. Lu, N. Mazet, B. Spinner (1996) Modelling of gas-solid reaction - coupling of heat and mass transfer with chemical reaction. Chem. Engng. Sci. 51(15); 3829-3845.

[27] F.Poyelle, J. J. Guilleminot, F. Meunier (1996) Analytical study of a gas-fired adsorptive air-conditioning system. ASHRAE Transactions. 102(1); 1128-1138.

[28] D. Stitou, V. Goetz, B. Spinner (1997) A new analytical model for solid-gas thermochemical reactors based on thermophysical properties of the reactive medium. Chemical Engng. and Processing. 51(15); 3829-3845.

[29] H. T. Chua, K. C. Ng, A. Malek, T. Kashiwagi, A. Akisawa, B. B. Saha (1999) Modeling the performance of two-bed, silica gel-water adsorption chillers. Int. J. Refrig. 22; 194-204.

[30] G. Restuccia and G. Cacciola (1999) Performances of adsorption systems for ambient heating and air conditioning. Int. J. Refrig. 22; 18-26.

[31] F. Poyelle, J. J. Guilleminot, F. Meunier (1999) Experimental tests and predictive model of an adsorptive air conditioning unit. Ind. Eng. Chem. Res. 38; 298-309.

[32] A. P. F. Leite, M. Daguenet (2000) Performance of a new solid adsorption ice maker with solar energy regeneration. Energy Conversion & Management. 41; 1625-1647.

[33] H. J. Huang, G. B. Wu, J. Yang, Y. C. Dai, W. K. Yuan, H. B. Lu (2004) Modeling of gas–solid chemisorption in chemical heat pumps. Separation and Purification Technology. 34;191-200.

[34] N. Douss, F. Meunier (1989) Experimental study of cascading adsorption cycles. Chem. Eng. Sci. 44; 225-235.

[35] L. Wade, P. Sywulka, M. Hattar, J. Alvarez (1990) High efficiency sorption refrigerator design. Advances in Cryogenic Engineering. 35; 1375-1382.

[36] P. Neveu, J. Castaing (1993) Solid-gas chemical heat pumps: Field of application and performance of the internal heat of reaction recovery process. Heat Recovery Systems & CHP. 13(3); 233-251.

[37] B. B. Saha, E. C. Boelman, T. Kashiwagi (1995) Computational analysis of an advanced adsorption refrigeration cycle. Energy. 20(10); 983-994.

[38] M. Pons, D. Laurent, F. Meunier (1996) Experimental temperature fronts for adsorptive heat pump applications. Appl. Thermal Engng. 16(5); 395-404.

[39] P. Satzger, F. Ziegler, D. Stitou, B. Spinner, Bernard; G. Alefeld (1996) Advanced sorption chillers for gas cooling. ASHRAE Transactions. 102(1); 1095-1100.

[40] S. Szarzynski, Y. Feng, M. Pons (1997) Study of different internal vapour transports for adsorption cycles with heat regeneration. Int. J. Refrig. 20(6); 390-401.

[41] R. E.Critoph (1998) Forced convection adsorption cycles. Appl. Thermal Engng.18; 799-807.

[42] R. Z. Wang, Y. X. Xu, J. Y. Wu, W. Wang (1998) Experiments on heat regenerative adsorption refrigerator and heat pump. Int. J. Energy Research; 22, 935-941.

[43] R. Z. Wang, J. Y. Wu, Y. X. Xu, Y. Teng, W. Shi (1998) Experiment on a continuous heat regenerative adsorption refrigerator using spiral plate heat exchanger as adsorbers. Appl. Thermal Engng. 18(1-2);13-23.

[44] M. Pons, F. Poyelle (1999) Adsorptive machines with advanced cycles for heat pumping or cooling applications. Int. J. Refrig. 22; 27-37.

[45] R. Z. Wang, J. Y. Wu, Y. X. Xu, W. Wang (2000) Performance researches and improvements on heat regenerative adsorption refrigerator and heat pump. Energy Conversion and Management. 42(2); 233-249.

[46] T. F. Qu, R. Z. Wang, W. Wang (2001) Study on heat and mass recovery in adsorption refrigeration cycle. Applied Thermal Engng. 21; 439-452.

[47] R. Z. Wang (2001) Adsorption refrigeration research in Shanghai Jiao Tong University. Renewable and Sustainable Energy Reviews. 5; 1-37.

[48] R. Z. Wang, (2001) Performance improvement of adsorption cooling by heat and mass recovery operation. Int. J. Refrig. 24; 602-611.

[49] R. G. Oliveira, V. Silveira Jr. (2002) The effects of operation and design variables on the specific cooling power of an advanced adsorption cycle for ice production powered by low temperature heat source. Proc. of Int. Sorption Heat Pump Conf. (ISHPC 2002). China.

[50] K. C. A. Alam, A. Akahira, Y. Hamamoto, A. Akisawa, T. Kashiwagi (2004) A four-bed mass recovery adsorption refrigeration cycle driven by low temperature waste/renewable heat source. Renewable Energy. 29; 1461-1475.

[51] R. G. Oliveira, V. Silveira Jr. R. Z. Wang (2005) Experimental Study of Mass Recovery Adsorption Cycles for Ice Making at Low Generation Temperature. Accepted for publication in Appl. Thermal. Engng.

[52] D. I. Tchernev (1978) Solar energy application of natural zeolites, in natural zeolite: occurrence, properties and use. Oxford: Pergamon Press, 479 p.

[53] J. J. Guilleminot, F. Meunier (1981) Etude expérimentale d'une glacière solaire utilisant le cycle zeolithe 13X+eau. Rev.

Gen. Thermique Fr. 239; 825-834.

[54] M. Pons, J. J. Guilleminot (1986) Design of an experimental solar-powered, solid-adsorption ice maker. J. Solar Energ. Trans. ASME. 108(4); 332-337.

[55] R. E. Critoph (2002) Carbon-ammonia systems-revious experience, current projects and challenges for the future. Proc. of the Int. Sorption Heat Pump Conf. (ISHPC 2002). China.

[56] R. E. Critoph (1993) Laboratory testing of an ammonia carbon solar refrigerator. Proc. of Solar World Congress (ISES). Hungary.

[57] M. Li, R. Z. Wang, Y. X. Xu, J. Y. Wu, A. O. Dieng (2002) Experimental study on dynamic performance analysis of a flat-plate solar solid-adsorption refrigeration for ice maker. Renewable Energy. 27; 211-221.

[58] M. Li, C. J. Sun, R. Z. Wang, W. D. Ca (2004) Development of no valve solar ice maker. Appl. Thermal Engng. 24; 865-872.

[59] E. J. Hu (1998) A study of thermal decomposition of methanol in solar powered adsorption refrigeration systems. Solar Energy. 62; 325-329.

[60] F. Buchter, Ph. Dind, M. Pons (2003) An experimental solar-powered adsorptive refrigerator tested in Burkina-Faso. Int. J. of Refr. 26; 79-86.

[61] A. Boubakri, M. Arsalane, B. Yous, L. Ali-Moussa, M. Pons, F. Meunier (1992) Experimental study of adsorptive solar powered ice makers in Agadir (Morocco)-1. Performance in actual site. Renewable Energy. 2(1); 7-13.

[62] A. Boubakri, M. Arsalane, B. Yous, L. Ali-Moussa, M. Pons, F. Meunier (1992) Experimental study of adsorptive solar powered ice makers in Agadir (Morocco)-2. Influences of meteorological parameters. Renewable Energy. 2(1); 15-21.

[63] C. Hildbrand, P. Dind, M. Pons, F. Buchter (2004) A new solar powered adsorption refrigerator with high performance. Solar Energy. 77; 311-318.

[64] N. M. Khattab A novel solar-powered adsorption refrigeration module. Appl. Thermal Engng 24 (2004) 2747–2760

[65] R. G. Oliveira (2004) Avaliação de um sistema de refrigeração por adsorção para produção de gelo, operando diferentes tipos de ciclo com baixas temperaturas de geração. Ph.D. Thesis. Dep. Food Engineering, School of Food Engineering, State University of Campinas; Brazil; 185 p.

[66] R. Z. Wang, M. Li, Y. X. Xu, J. Y. Wu (2000) An energy efficient hybrid system of solar powered water heater and adsorption ice maker. Solar Energy. 68(2); 189-195.

[67] R. Z. Wang, Y. X. Xu, J. Y. Wu, M. Li, H. B. Shou (2002) Research on a combined adsorption heating and cooling system. Appl. Thermal Engng. 22; 603-617.

[68] Ph. Grenier, J. J. Guilleminot, F. Meunier, M. Pons (1988) Solar powered solid adsorption cold store. J. Solar Energ. Trans. ASME. 110(3); 192-197.

[69] B. B. Saha, A. Akisawa, T. Kashiwagi (2001) Solar/waste heat driven two-stage adsorption chiller: the prototype. Renewable Energy. 23; 93–101.

[70] R. Z. Wang, J. Y. Wu, Y. X. Xu, W. Wang (2001) Performance researches and improvements on heat regenerative adsorption refrigerator and heat pump. Energy Conversion & Management. 42; 233-249.

[71] Y. L. Liu, R. Z. Wang, Z. Z. Xia (2005) Experimental study on a continuous adsorption water chiller with novel design. Int. J. Refrig. 28(2); 218-230.

[72] Z. Z. Xia, R. Z. Wang, J. Y. Wu, D. C. Wang (2003) New type of effective adsorption chiller adopt separate heat pipe (in Chinese). Chinese Patent 200410025398.0.

[73] T. Nuñez, W. Mittelbach, H. M. Henning (2004) Development of an adsorption chiller and heat pump for domestic heating and air-conditioning applications. Proc. of the 3rd Int. Conf. on Heat Powered Cycles (HPC 2004). Cyprus.

[74] G. Restuccia, A. Freni, S. Vasta, Y. Aristov (2004) Selective water sorbent for solid sorption chiller: experimental results and modeling. Int. J. Refrig. 27; 284-293.

[75] M. Z. Ismail, D. E. Angus, G .R. Thorpe (1991) The performance of a solar-regenerated open-cycle desiccant bed grain cooling system. Solar Energy, 46(2); 63-70.

[76] T. F. N. Thoruwa, A. D. Grant, J. E. Smith, C. M. Johnstone (1998) A solar-regenerated desiccant dehumidifier for the aeration of stored grain in the humid tropics. Journal of Agr. Engng Res. 71(3); 257-262.

[77] H. M. Henning, T. Erpenbeck, C. Hindenburg, I. S. Santamaria (2001) The potential of solar energy use in desiccant cooling cycles. Int. J. of Refr. 24; 220-229.

[78] S. M. Lu, W. J. Yan (1995) Development and experimental validation of a full-scale solar desiccant enhanced radiative cooling. Renewable Energy. 6(7); 821-827.

[79] The Climasol Project (2005) In: http://www.raee.org /climasol , last access 14/05/2005.

[80] L. Z. Zhang (2000) Design and testing of an automobile waste heat adsorption cooling system. Appl. Thermal Engng. 20; 103-114.

[81] L. W. Wang, J. Y. Wu, R. Z. Wang, Y. X. Xu, S. G. Wang (2003) Experimental study of a solidified activated carbon-methanol adsorption ice maker. Appl. Thermal Engng. 23; 1453-1462.

[82] S. G. Wang, R. Z. Wang (2005) Recent developments of refrigeration technology in fishing vessels. Renewable Energy. 30, 589–600.

[83] Z. Tamainot-Telto, R. E. Critoph (1997) Adsorption refrigerator using monolithic carbon ammonia pair. Int. J. of Refr. 20(2); 146-155.

[84] L. W. Wang, R. Z. Wang, J. Y. Wu, K. Wang, S. G. Wang (2004) Adsorption ice makers for fishing boats driven by the exhaust heat from diesel engine: choice of adsorption pair. Energy Conversion and Management. 45; 2043-2057.

[85] Y. Z. Lu, R. Z. Wang, S. Jianzhou, Y. X. Xu, J. Y. Wu (2004) Practical experiments on an adsorption air conditioner powered by exhausted heat from a diesel locomotive. Appl. Thermal Engng. 24; 1051-1059.

[86] S. Jiangzhou, R. Z. Wang, Y. Z. Lu, Y. X. Xu, J. Y. Wu (2002) Experimental investigations on adsorption air-conditioner used in internal-combustion locomotive driver-cabin. Appl. Thermal Engng. 22; 1153-1162.

[87] Z. Tamainot-Telto, R. E. Critoph (2003) Advanced solid sorption air conditioning modules using monolithic carbon–ammonia pair. Appl. Thermal Engng. 23; 659-674.

[88] HIJC USA Inc. (2005) Waste heat adsorption chiller substitute absorption. In: http://www.adsorptionchiller. bigstep.com/homepage.html, last access in 14/05/2005.

[89] P. Garland, D. Hinrichs, M. Cowie (2005) Integrating CHP into commercial buildings. In: http://www.earthscan.co.uk/news/article/mps/UAN/67/v/4/sp/332882698304342120264, last access in 14/05/2005.

[90] Rational supply of power, heat and cooling in the malteser hospital St. Johannes in Kamenz (2005) In: http://www.malteser-krankenhaus-kamenz.de/englisch/index.htm, last access in 14/05/2005.

[91] R. Z. Wang, X. Q. Kong, J.Y. Wu, Y. Huangfu, D.W. Wu (2005) Performance research of a micro CCHP system with adsorption chiller. Proc. of the International Sorption and Heat Pump Conference (ISHPC 2005). USA.

[92] A. Maranthan (2002) Optimization of Integrated Microturbine and Absorption Chiller Systems in CHP for Buildings Applications. Ph.D. Thesis. Dep. Mechanical Engineering, University of Maryland; USA; 130 p.

[93] F. Meunier (1998) Solid sorption heat powered cycles for cooling and heat pumping applications. Appl. Thermal Engng. 18; 715-729.

[94] R. E. Critoph (2000) The use of thermosyphon heat pipes to improve the performance of a carbon–ammonia adsorption refrigerator. Proc. of the IV Minsk Int. Seminar - Heat Pipes, Heat Pumps, Refrigerators; Belarus.

[95] L. L. Vasiliev, D. A. Mishkinis, A. A. Antukh, L. L. Vasiliev Jr. (1999) A solar and electrical solid sorption refrigerator. Int. J. Therm. Sci. 38, 220-227.

[96] Z. Z. Xia, R. Z. Wang, J. Y. Wu, L. W. Wang (2004) Compound alternate heat pipe reactor powered by waste heat (in Chinese). Chinese Patent 200410018291.3.

[97] L. W. Wang, R. Z. Wang, J. Y. Wu (2003) Separate heat pipe adsorption ice maker for fishing boats (in Chinese). Chinese Patent 200310108924.5.

[98] S. Dunne (1996) Carousel heat exchanger for sorption cooling process. US Patent, 5 503 222.

[99] P. Bou, J. J. Guilleminot, M. Pons (1996) Composite actif à structure feuilletée comprenant un agent actif sous forme de granules. Elf Aquitaine Patent, 96 12762.

[100] F. Meunier, S. C. Kaushik, P. Neveu, F. Poyelle (1996) A comparative thermodynamic study of sorption systems: second law analysis. Int. J. Refrig. 19(6); 414-421.

[101] D. I. Tchernev, D. T. Emerson (1988) High-efficiency regenerative zeolite heat pump. ASHRAE Transactions. 94(2); 2024-2032.

[102] D. Miles, S. Shelton (1996) Design and testing of a solid-sorption heat-pump system. Appl. Thermal Engng, 16; 389-394.

[103] L. Wade, E. Ryba, C. Weston, J. Alvarez (1992) Test performance of a 2 W, 137 K sorption refrigerator. Cryogenics. 32(2); 122-126.