A REVIEW: FUTURE OF THE ADSORPTION WORKING PAIRS IN COOLING

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This study aims to draw a map for the application of adsorption pairs in cooling. The study introduces a classification and a comparison for the working pairs in order of its use. The comparison is on the basis of the limits of use as maximum COP, driving temperature, evaporation temperature and SCP are introduced. The study also introduces a review for the most promising adsorption cooling pairs. Finally the study decided that the future of adsorption cooling could be more popular as it will offer new answers for the existing challenges.

Keywords: adsorbents, absorption system, cooling system

Nomenclature

COP	coefficient of performance.
C	adsorption capacity of the adsorbent, g $_{\text{refrigerant}}$/g $_{\text{adsorbent}}$.
K	constant.
n	constant.
P	adsorption pressure, kPa.
q_{st}	isosteric heat of adsorption, W/kg.
SCP	specific cooling power.
T	adsorbent temperature, K.
T_{ads}	adsorption temperature, °C.
T_b	normal boiling temperature, °C.
T_d	driving temperature, °C.
T_e	evaporation temperature, °C.
T_{sat}	saturation temperature corresponding to the refrigerant pressure, K.
X	refrigerant concentration, kg $_{\text{refrigerant}}$ /kg $_{\text{adsorbent}}$.
x_o	refrigerant concentration at saturation conditions, kg $_{\text{refrigerant}}$ /kg $_{\text{adsorbent}}$.

1. Introduction

Adsorption refrigeration systems have received a lot of attention due to their effective cold production based on waste heat or solar energy utilization. Adsorption refrigeration systems have a number of advantages in comparison with the conventional refrigeration machines. When compared with vapor compression refrigeration systems, adsorption refrigeration systems are environmentally friendly and they can utilize the low-grade waste heat or renewable energy as the main driving energy and thus have a large energy saving potential. In addition, they have a higher reliability because it has no moving parts.

The basic adsorption cycle for cooling consists of four processes represented in Fig. 1. In the first one A–B, the adsorbent is heated until the pressure reaches a level that enables desorption of refrigerant (state B). During process B–C addition of heat results in desorption of vapor refrigerant, which condenses in an aircooled condenser. At state C, when the adsorbent reaches its maximum temperature, temperature starts to decrease. Cooling of the adsorbent provokes a drop of pressure in the collector (process C–D). Meanwhile, the liquid refrigerant is transferred into the evaporator the adsorbent continues to decrease in temperature and pumps the liquid refrigerant, which evaporates and extracts heat from the evaporator (process D–A) generating a cooling process inside the chamber [Lemmini and Errougani (2007)].

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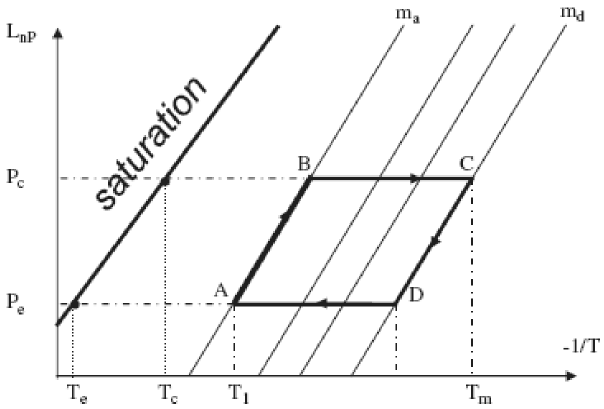

Fig. 1. The ideal of adsorption cooling in clapeyron diagram.

2. Working Adsorption Cooling Pairs

Adsorption pair means the pair which consists of adsorbent and refrigerant. The adsorption working pair is the vital part in the adsorption refrigeration cycle. The selection of any pair of adsorbent–adsorbate for refrigeration applications depends on certain desirable characteristics of their constituents. These characteristics range from their thermodynamic and chemical properties to their physical properties and even to their costs or availability.

The adsorbate or refrigerant should have the following properties [Alghoul *et.al*.(2007)]:

1. Evaporation temperature below 0 °C.
2. Small molecular size to enable it to be adsorbed into the adsorbent.
3. High latent heat of vaporization and low specific volume.
4. Thermally stable with the adsorbent at the cycle operating temperature ranges.
5. Non-toxic, non-corrosive and non-flammable.
6. Low saturation pressures (above atmospheric) at normal operating temperature.

The important considerations influencing the choice of a suitable adsorbent are [Alghoul *et.al*.(2007)]

1. Adsorption of large amount of the adsorbate under low temperature conditions.
2. Desorption of most of the adsorbate when exposed to thermal energy.
3. Possession of high latent heat of adsorption compared to sensible heat.
4. No deterioration with age or use.
5. Non-toxic and non-corrosive.
6. Low cost and widely available.

According to the basic principle and working characteristics of the adsorption refrigeration cycle, actually, there are no working pairs to completely meet the requirements mentioned above. But there are many commonly used working pairs which closely meet these requirements [Wang et.al. (2010)].

The governing equation for the adsorption relation between the adsorption working pair is the Dubinin–Radushkevich (D-R) Eq.(1)[Critoph (1996)]:

$$X = x_{\circ} \exp\left[-k \left(\frac{T}{T_{sat}} - 1 \right)^{n} \right] \tag{1}$$

The adsorption process is divided into physical adsorption and chemical adsorption. Physical adsorption is caused by van der Walls force between the molecules of the adsorbent and the adsorbate. Physical adsorbents with mesopores can adsorb consecutive layers of adsorbate, while those with micropores have the volume of the pores filled with the adsorbate. Physical adsorbents develop the selectivity to the adsorbate after the former undergo specific treatments, like react under a gas stream or with certain agents. The kind of treatment will depend on the type of sorbents [Wang *et.al*. (2009)].

Chemical adsorption is caused by the reaction between adsorbates and the surface molecules of adsorbents. Electron transfer, atom rearrangement and fracture or formation of chemical bond always occurs in the process of chemical adsorption. Only one layer of adsorbate reacts with the surface molecules of chemical adsorbent. The adsorbate and adsorbent molecules after adsorption never keep their original state. Composite adsorbents started to be studied about 20 years ago, and they aimed to improve the heat and mass transfer performance of the original chemical adsorbents. This kind of adsorbent is usually obtained by the combination of a chemical adsorbent and a porous medium, that can be or not a physical adsorbent [Wang *et.al*. (2009)].The study will introduce a review for the already applied cooling systems using adsorption pairs. In order to make the choice of any intended working pair, the study will introduce a comparison between pairs on the basis of best limits for an already adsorption cooling systems. The comparison will demonstrate the maximum COP reached for every pair and the minimum evaporation temperature and minimum driving temperature.

2.1. *Physical adsorption*

2.1.1. *Activated carbon/ammonia*

Activated carbons are made by pyrolizing and carbonizing source materials, such as coal, lignite, wood, nut shells and synthetic polymers, at high temperatures (700 to 800°C). Activated carbons are available in many forms including powders, micro-porous, granulated, molecular sieves and carbon fibers. Generally, the activated carbon in the powdered form (15 to 25 mm particles) is used for adsorption of liquids and in granulated (sieved granules of 4 to 20 mesh or about 3 mm to 0.8 mm diameter) or pellet (extruded pellets of 4 to 6 mm length) forms for air purification and gas separation. Activated carbon fibers (fiber diameter of 7 to 15μm) are made by carbonizing synthetic fibers [Srivastava and Eames (1998)].

Ammonia has a relatively high latent heat of about 1365 kJ/kg at -30 °C and the maximum adsorption quantity in activated carbon is 0.29 g/g [Wang *et.al*.(2006)]. Whoever ammonia has the disadvantage of toxicity and corrosive. The heat of adsorption for carbon-ammonia pair is in range of 2000 to 2700 kJ/kg [Srivastava and Eames (1998)]. Desorption pressure of the activated carbon–ammonia reaches 1.6 MPa so that high pressure. The relatively high pressure enhances the mass transfer of the activated carbon–ammonia system and shortens the adsorption time and then the SCP (specific cooling power) of the system rises [Wang *et.al*. (2010)].

Tamainot-Telto et al. [Tamainot- Telto and Critoph (1997)], studied the adsorption refrigerator using monolithic carbon-ammonia pair. The experimental results demonstrated that the maximum SCP the COP were 60 W/kg $_{\text{carbon}}$ and 0.12, respectively. Tamainot-Telto et al. [Tamainot-Telto *et.al*. (2009)], investigated Carbon–ammonia pairs for adsorption refrigeration applications. The simulation results of 26 various activated carbon–ammonia pairs for three cycles (single bed, two-bed and infinite number of beds). The carbon adsorbents investigated were mainly coconut shell and coal based types in multiple forms: monolithic, granular, compacted granular, fiber, compacted fiber, cloth, compacted cloth and powder and the driving temperature varied from 80 °C to 200 °C. Considering a two-bed cycle, the best thermal performances based on power density were obtained with the monolithic carbon, with a driving temperature of 100 °C; the cooling production was about 66 MJ/m (COP = 0.45) and 151 MJ/m (COP = 0.61) for ice making and air conditioning respectively.

Critoph [Critoph and Metcalf (2004)], reached to 0.35 COP and 2000 W/kg SCP with a plate type generator at 200 °C driving temperature and 15 °C evaporation temperature. The minimum cycle time was 12 s.

2.1.2. *Activated carbon/methanol*

Activated carbon and methanol is one of the most common working pair due to the large adsorption quantity and lower adsorption heat, which is about 1800–2000 kJ/kg. However, activated carbon/methanol has the disadvantage of operating under sub-atmospheric pressure [Srivastava and Eames (1998)].The maximum adsorption quantity in activated carbon is 0.45 g/g and the latent heat at -30 °C is about 1229.1 kJ/kg °C [Wang *et.al*.(2006)]. However, the methanol decomposes at 120 °C through either a dehydrogenation or a dehydration mechanism to form formaldehyde (HCHO) or dimethyl ether (CH_3OCH_3) [Wang *et.al*. (2010); HU (1998)]. The aluminum alloy was found to have a stronger catalytic effect on the decomposition reaction than copper [HU (1998)].

El-Sharkawy et al. [El-Sharkawy *et.al*. (2009)], studied the adsorption of methanol onto carbon based adsorbents. The study presented the isothermal characteristics of methanol adsorption onto two specimens of activated carbons namely Maxsorb III and Tsurumi activated charcoal. For the evaporator temperature of 15 °C, the Maxsorb III can adsorb methanol of 1.2 g/g within about 160 min. The change of SCP and COP with regeneration temperatures for Maxsorb III/methanol, activated charcoal/methanol, LH/methanol, DEG/methanol and AC-35/methanol pairs was studied. The maximum COP was 0.78 with Maxsorb III/methanol at regeneration temperature of 90 °C. Theoretical results showed that the superiority of Maxsorb III/methanol pair among other carbonaceous adsorbent/methanol pairs for both of air conditioning and ice-making applications. A system was studied by Wang et al. [Wang *et.al*. (2003)], using solidified activated carbon as a bed was had a COP of 0.125 and SCP of 16 W/kg at a cycle time of 56 min.

2.1.3. *Activated carbon/ethanol*

The performance of refrigeration system using activated carbon and ethanol was studied by many researchers. Using Maxsorb III as an activated carbon El-sharkawy *et al*. [El-Sharkawy *et.al*.(2008)] introduced a solar powered adsorption cooling system. The capacity of Maxsorb III was estimated experimentally to be1.2 g/g with an adsorption temperature from 20 to 60 °C and the driving temperature was 80 °C. The COP of the system was about 0.8 at evaporation temperature of 15 °C. The specific cooling effect was about 420kJ/kg at an evaporator temperature of 7 °C.

Activated carbon fibers and ethanol as an adsorption pair was introduced by Saha et al. [Saha et.al. 2007a; 2007b]. The driving temperature was in between 60 and 95 °C. The COP reached to about 0.6 with a cycle time of 600-700 s.

2.1.4. *Silica gel/water*

The silica gel is a type of amorphous synthetic silica. It is a rigid, continuous net of colloidal silica, connected to very small grains of hydrated SiO_4. The pore diameters of common silica gel are 2, 3 nm (A type) and 0.7 nm (B type), and the specific surface area is about 100–1000 m^2/g [3].

Water could be considered a very good refrigerant but it has the disadvantage of impossibility to get an evaporation temperature less than 0 °C. The heat of adsorption for silica gel/water pair is about 2800 kJ/kg [6]. One disadvantage of silica gel/water working pair is the low adsorption quantity, which is about 0.2 g/g [5]. Chen et al. [17], studied experimentally a compact silica gel–water adsorption chiller without vacuum valves. Microporous silica gel with diameter from 0.5 to 1.5 mm was used. A novel heat recovery process was fulfilled after the mass recovery-like process to improve the coefficient of performance (COP). The cooling power and COP were 9.60 kW and 0.49 respectively when the driving temperature and chilled water outlet temperature were 82 and 12.3 °C, respectively. The optimal cycle time, mass recovery-like time and heat recovery time were 720, 80 and 20 s, respectively. Ruud et al. [18], investigated waste heat driven silica gel/water adsorption cooling in trigeneration. The system was tested as to the power delivered at 12 °C. The average cooling power was 3.6 kW with a SCP of 208 W/kg. The thermal efficiency, COP, was 0.62.

2.1.5. *Zeolite/water*

Zeolite is a type of aluminasilicate crystal composed of alkali or alkali soil. The porosity of the aluminasilicate skeletal is between 0.2 and 0.5. There are about 40 types of natural zeolites, and the main types for adsorption refrigeration are chabazite, sodium chabazite, cowlesite and faujasite. About 150 types of zeolites can be artificially synthesized, and they are named by one letter or a group of letters, such as type A, type X, type Y, type ZSM, etc. Artificially synthesized zeolite molecular sieves have micropores with uniform size, and different sizes can be obtained by different manufacturing methods. 4A, 5A, 10X and 13X zeolite molecular sieves are the main types used for adsorption refrigeration. The adsorption temperature of zeolite pairs is about 250–300 °C [6]. The heat of adsorption for the Zeolite/water is in range of 330-4200 where Natural zeolites have lower values than synthetic zeolites [5]. The maximum amount of water could be adsorbed by zeolit were estimated by Ismail [19] to be 0.12 g/g using zeolite 13X.

Wang et al. [20], investigated design and performance prediction of a novel zeolite–water adsorption air conditioner. A novel adsorption air conditioner supplied 8–12 °C chilled water for the fan coil. The system was driven by 350–450 °C exhaust gas. The designed refrigerating power and COP were 5 kW and 0.25 respectively. The refrigerating power of the machine was up to 10 kW with an evaporating temperature of 6.5 °C. The cycle time was 1320 s and the SCP reached 200 W/kg.

2.2. *Chemical adsorption working pairs*

The thermo-chemical refrigeration offers some advantages with regard to the conventional systems: low temperatures and dissociation pressures, adsorbent vapor rectification is not necessary and it is possible cooling with air. Their main disadvantages are the intermittent operation and the low thermal conductivity of the solids [21].

2.2.1. *Metal chlorides/ammonia*

The metal chlorides for adsorption refrigeration are mainly calcium chloride, strontium chloride, magnesium chloride, barium chloride and nickel chloride [21]. The disadvantage of metal chlorides/ammonia as working pair is mainly related to the salt swelling and agglomeration during adsorption, which compromise the heat and mass transfer [5].

Duenas et al. [22], introduced a Dynamic study of the thermal behavior of solar thermochemical refrigerator: barium chloride-ammonia for ice production and the COP were about 0.63. The evaporation temperature was -10 °C and the driving temperature was decreased to 52 °C.

2.2.2. Metal hydrides/hydrogen

Metal hydrides absorb hydrogen gas and have been used for hydrogen storage. When hydrogen is adsorbed by a hydride, an exothermic reaction occurs and heat is liberated. When hydrogen gas is desorbed from a hydride, an endothermic reaction occurs, providing significant cooling. There are 26 known adsorbed metal hydrides for hydrogen [23]. Specially developed porous metal hydrides or misch metal matrix alloys, containing Ni, Fe, La, Al, H have very high rates of sorption to hydrogen [5].

Metal hydrides offer a wide range of potential applications because the existence of hydrides with equilibrium temperatures (for 1 bar equilibrium pressure) between -113 °C and 527 °C and above. The disadvantage of the metal hydrides/hydrogen is the weight of the system, which is nearly twice as high as for a system working with evaporator and condenser.

Three different schemes of metal hydride adsorption cooling applications were presented and compared based on theoretical evaluations. The single and double stage devices showed reasonable performances. Cycle times of about 300-600 s could be obtained with these devices. This SCP was about 100-200 W/kg for single stage or 150-300 W/kg for double stage. The maximum COP of a metal hydride/hydrogen cooling system were 0.83 with an evaporation temperature of 3 °C. The driving temperature was 85-215 °C. The minimum evaporation temperature could be -50 °C [24]. The maximum amount of hydrogen which could be adsorbed in metal hydrides is 0.073 g/g and that with MgH_2 at % 1 Al and with a 0.6 adsorption pressure [25].

2.2.3. Metal oxides/water

An example for the metal oxides and water in refrigeration is the reaction between magnesium oxide and water as in the following reaction. A reaction towards the right-hand side is exothermic MgO hydration and the reaction toward the left side is endothermic [26].

MgO (solid) + H_20 (gas) $\leftrightarrow$ $Mg(OH)$ (solid), $\Delta H = -81.02$ kJ/mol.

Kato [27], reported that the hydration resulted at an evaporation temperature of 100 °C with a driving temperature of 200-300 °C and a vapor Pressure of 101 kPa. The total time of the cycle was about 240 min.

2.3. ***Composite adsorbents***

The first reason to improve heat and mass transfer performance of chemical adsorbents is to increase the performance of the adsorption process. Salt swelling reduces the heat transfer, and salt agglomeration reduces the mass transfer. Therefore, the addition of chemical adsorbents such as expanded graphite which have a porous structure and high thermal conductivity to a metallic salt will help to raise the heat transfer performance [28, 29]. The second reason to use additions to the chemical adsorbents is the trial to increase its permeability [30].

The composite adsorbents made from porous media and chemical sorbents are commonly a combination of metal chlorides and activated carbon, or activated carbon fiber, or expanded graphite, or silica gel or zeolite [5].

2.3.1. ***Silica gel and chlorides/water***

Aristov et al. [30], tested $CaCl_2$ and LiBr as a salts with a different micro and mesopores of silica gel as an adsorbent and water as an adsorbate to introduce a new composite adsorption cooling pair. The results showed that the water adsorption capacity could be reached to 0.75 g/g. The adsorption temperature was 70-120 °C and the maximum pressure was about 10 kPa and the minimum pressure of the adsorption cycle was 1 kPa. The evaporation temperature was 7 °C with a COP in range of 1.1-1.65.

2.3.2. *Silica gel and chlorides/methanol*

The capacity of Silica gel and chlorides to methanol adsorption could be reached to 0.8 g/g [31]. Maggio et al. [32], introduced a simulation of solid adsorption ice-maker using a composite adsorption pair of lithium chloride and silica gel/methanol. The results showed that the maximum COP of 0.33 and the maximum daily ice production of 20 kg m^{-2} could be obtained. The minimum evaporation temperature was -10 °C and the driving temperature was in range of 47-57 °C. The maximum adsorption cycle pressure was about 20 kPa and the minimum pressure was about 3.5 kPa and the cycle time was 24 hours.

2.3.3. *Chlorides and porous media/ammonia*

Oliveira et al. [33], evaluated the cooling performance of a consolidated expanded graphite calcium chloride reactive bed. SCP was higher than 1000W/kg and COP was about 0.35. The capacity of the bed was 0.8g/g and the cycle time was about 5min. The evaporation temperature was between -20 to -30°C and the driving temperature was about 150°C.

A lab scale adsorption chiller worked using porous matrix modified by active salt as an adsorbent and ammonia as an adsorption pair was introduced. Composite material (45 weight % $BaCl_2$/vermiculite) could provide effective operation of the chiller using a low potential heat source of 80–90°C to give COP about 0.54 and SCP ranging from 300 to 680W/kg. The evaporation temperature was 10°C and the time of the cycle is in rage 360-720s. The maximum pressure of the cycle was 15bar and the minimum pressure was 5bar. The maximum adsorption capacity was about 0.239 [34, 35].

The performance of an ice maker using composite adsorbents made by the $CaCl_2$ and activated carbon, were researched by Wang [36]. Activated carbon was used as a type of porous additive, where a mass ratio between $CaCl_2$ and activated carbon was 4:1. The ice maker showed a COP and a SCP of 0.35 and 493.2W/kg respectively with a cycle time of 50 min. The evaporation temperature was about -15°C and the adsorption temperature was about 117.5°C.

2.3.4. *Zeolite and foam aluminum/water*

The performance of the adsorption refrigeration system works with a composite zeolite and foam aluminum/water as an adsorption pair was studied by Peng Hu [37]. The calculations showed that, with a 250 °C driving temperature and 10 °C evaporation temperature the COP could be reached to 0.55. The SCP could be reached to 500 W/kg with a cycle time of 20 min and the maximum capacity was about 0.22 g/g.

3. Comparison between Working Pairs

To choose the appropriate pair in adsorption cooling applications the running conditions and the aim of the application should be taken into account. For example when using the adsorption pair in solar cooling the important parameter governing the choice is the driving temperature as it should be the minimum allowable temperature. The most important running conditions are the driving temperature, evaporation temperature and COP. Table 1 introduces a comparison between the working adsorption pairs on the basis of the best reached operating conditions. The comparison covers the already constructed systems and conducted the best results of them. For every pair the running conditions were brought from existing systems and compared together to introduce the best. For every Raw in the table the shown data is not for one system but it is brought from many systems to get the limits of using the pair in cooling application.

Table 1. Comparison between the adsorption working pairs.

Working pair		COP	T_e °C	T_d °C	SCP W/kg
Physical adsorbent	Activated carbon/ammonia	0.61	-5	100	2000
	Activated carbon/methanol	0.78	15	90	16
	Activated carbon/ethanol	0.8	3	80	N.A
	Silica gel/water	0.61	12	82	208
	Zeolite/water	0.25	6.5	350	200
Chemical adsorbent	Metal chloride/ ammonia	0.6	-10	52	N.A
	Metal hydrides/hydrogen	0.83	-50	85	300
	Metal oxides/water	N.A	100	200	78
Composite adsorbents	Silica gel and chlorides/water	1.65	7	70	N.A
	Silica gel and chlorides/methanol	0.33	-10	47	N.A
	Chlorides and porous media/ammonia	0.35	-15	117.5	493.5
	Zeolite and foam aluminum/water	0.55	10	250	500

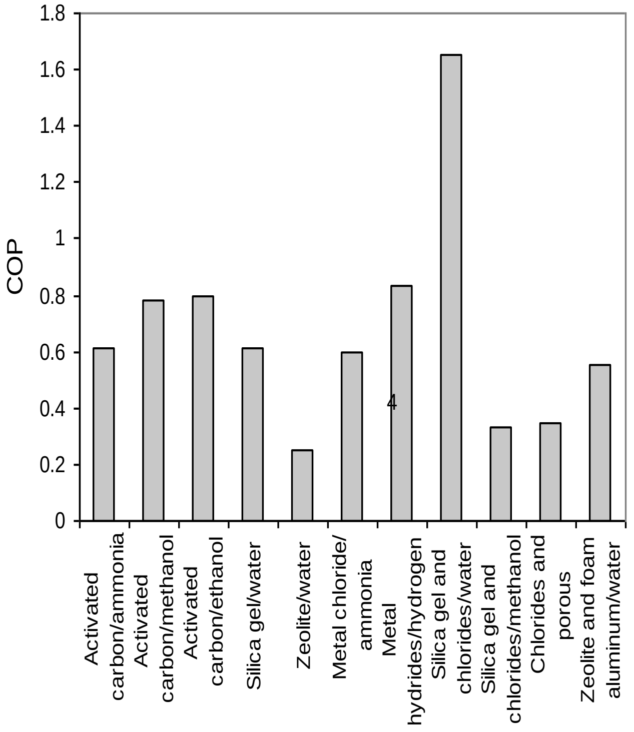

Fig. 2. Coefficient of performance for working pairs.

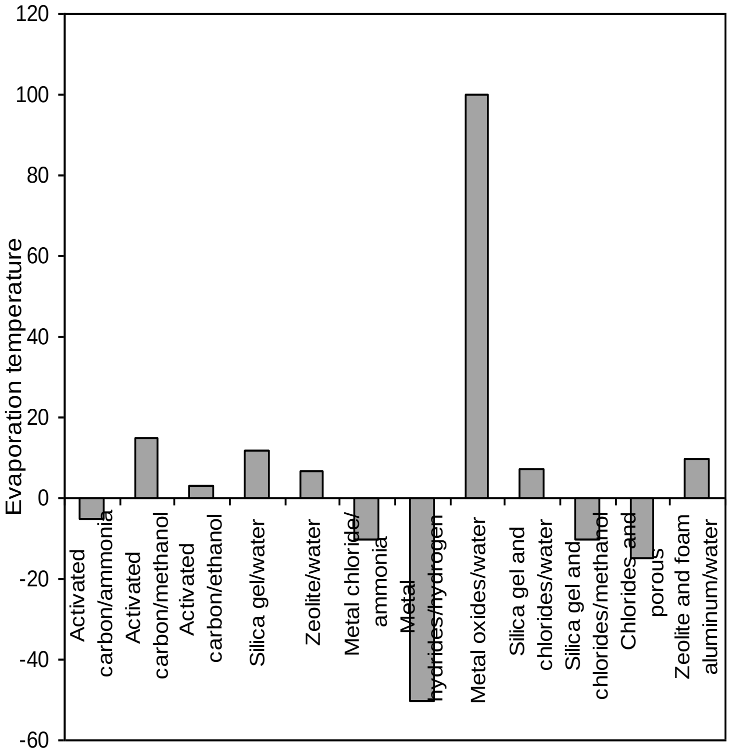

Fig. 3. Evaporation temperature for the working pairs.

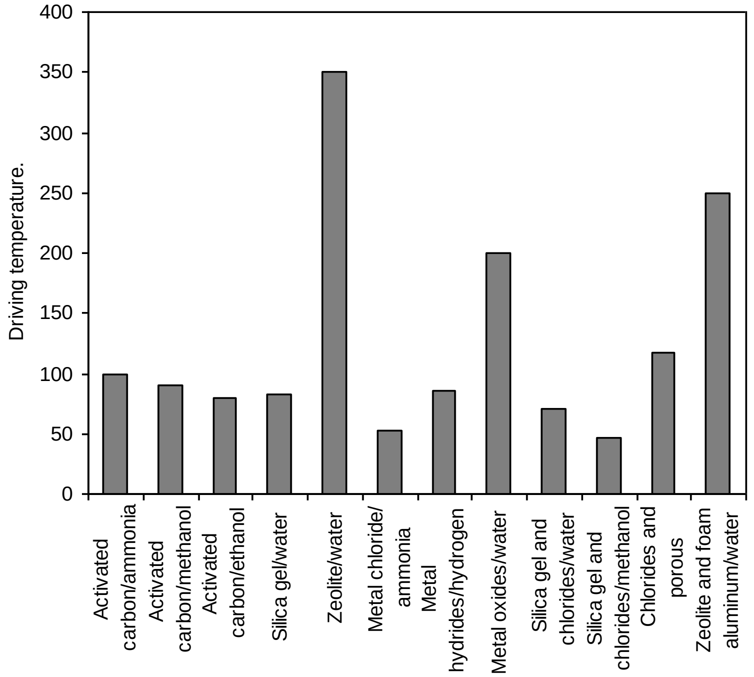

Fig. 4. Driving temperature for the working pairs.

4. New Adsorption Pairs

It is clear from the previous review about the adsorption pairs that the adsorption application in the field of cooling is still not an efficient way and is need for more development in many ways to improve its performance and extend its area of application. One of this ways is to introduce new pairs and investigate its characteristics in adsorption cooling. The Dubinin–Astakhov adsorption isotherm model usually uses to describe isotherms data within an acceptable error ranges. The most important data to estimate the suitability of the adsorption pair in cooling applications conditions are the adsorption cooling system is the temperature of evaporation, isosteric heat, regeneration temperature and the capacity of adsorption pair. So, here the study will introduce a survey about the new studied adsorption pairs concerning on the thermodynamic characteristics of adsorption.

4.1. *Activated carbon/hydrogen*

The characteristics of hydrogen adsorption on activated carbon were experimentally studied by Chen [38], Yoshitsugu [39]. The conventional activated carbon, graphite nanofiber and single walled carbon nanotube, Litchi trunk was activated by potassium hydroxide under N_2 or CO_2 atmosphere. Nanoparticles of palladium were impregnated in the prepared activated carbon. The maximum hydrogen adsorption capacity was 0.0289 g/g at -196 °C under 0.1 MPa. With 10% Palladium the adsorbent capacity of hydrogen could be reached to 0.055g/g under a pressure up to 6 MPa at 30 °C. The isosteric heat was in a range of 5.6–7.9 kJ/mol for the pair at -196 to -183 °C.

4.2. *Zeolite/CO_2*

The thermodynamic adsorption properties of CO_2 with zeolite were studied by Firas [40]. Potassium chabazite (KCHA), sodium-chabazite (NaCHA) and lithium-chabazite (LiCHA) powders were used to estimate the optimum conditions for CO_2 adsorption. The LiCHA introduced the best results according to the other adsorbents in adsorption capacity. The adsorption capacity of CO_2 in LiCHA could be reached to about 0.27 g/g under a pressure of 100 kPa and at a 0 °C and it was 0.24 g/g for NaCHA. The isosteric heat was the lowest magnitude with NaCHA as it was 40.8 kJ/mol where, it was about 43.5 kJ/mol with LiCHA for the temperature of 0 °C. The evaporation temperature of CO_2 is -78.51 °C. Zhong et al. [41] introduced a theoretical model for CO_2 as a refrigerant with some adsorbent. The model calculated COP of the refrigerant adsorption system. With zeolite as an adsorbent the COP was very low as it was about 0.044 with a 200 °C generating temperature and -5 °C evaporating temperature.

4.3. *Zeolite/N_2*

According to Firas [40], nitrogen has the ability to be adsorbed by zeolite. As the normal oiling temperature of nitrogen is -195.8 °C it can be considered a refrigerant. The characteristics of adsorption of zeolite with nitrogen were introduced. The adsorption capacity of chabazite was 0.04 g/g under a pressure of 100 kPa and 0 °C. The isosteric heat was decreased to 12.2 kJ/mol.

4.4. *Activated carbon fibers/N_2*

A pair of Iodine doped activated carbon fibers heated at 673 K for 2 hours as an adsorbent and nitrogen as an adsorbate was studied by Chelo [42] to estimate its adsorption characteristics. The adsorption capacity of nitrogen was found to be about 0.75 g/g at -196 °C. The isosteric heat was to be about 11.7 kJ/mol. Activated carbon fibers without Iodine was also studied with nitrogen as an adsorption pair. The results for activated carbon fibers without Iodine showed the same amount of isosteric heat and more adsorption capacity than that for activated carbon fibers with Iodine (0.8 g/g).

4.5. *Activated carbon/N_2*

The adsorption characteristics of beads activated carbon as an adsorbent and nitrogen as an adsorbate were introduced by Shen et al. [43]. Adsorption equilibrium for N_2 was measured at different temperatures and pressures. The highest adsorption capacity was 0.00756 g/g at 30 °C adsorption temperature and 100 kPa adsorption pressure. The isosteric heat magnitude was also determined to be 17.5 kJ/mol.

4.6. *Activated carbon/Diethyl Ether*

Granular activated carbon and diethyl ether was introduced as an adsorption pair by Al-Ghouti [44]. The normal Boiling temperature of diethyl ether ($(C_2H_5)_2O$) is 34.45 °C. The isosteric heat of the pair was found to be 45.84kJ/mol and the time of equilibrium adsorption was ranged from

45 to 20 minutes as adsorption temperature was varied from 26 to 50 °C. Experimentally the adsorption capacity of the diethyl ether on activated carbon at 26, 35, and 50 °C were 1.18, 1.63, and 1.39 mg/g, respectively at 10 kPa.

4.7. *Activated carbon/R134a*

The adsorption characteristics of activated carbon and R134a (1, 1, 1, 2-tetrafluoroethane $C_2H_2F_4$) had been widely researched theoretically and theoretically by many researchers [45, 46]. Using Maxsorb III labeled MSC-30 as an adsorbent with a measured surface area of 3150 m^2/g and a micropore volume of $17.0*10^{-4}$ m^3/kg and a 99.99% pure R134a as an adsorbate. The minimum isosteric heat for the pair was estimated to be about 21 kJ/mol. The maximum capacity for activated carbon of R134a was 2 g/g at 30°C isotherms adsorption at a pressure of 800 kPa. At 25°C the time of adsorption was estimated to be 1200 s. The normal boiling temperature of R134a is -26.55 °C and the molecular weight is 102.03.

4.8. *Activated carbon/R507A*

Maxsorb III labeled MSC-30 and 99.99% pure R507A (1, 1, 1-trifluoroethane $C_2H_3F_3$) was used as an adsorption pair. The R507a is a mixture of R125 and R134a in a fraction weight of 50% to 50% and its normal boiling point is -47.1 °C. When the isotherms adsorption temperature was 20 °C, the Maxsorb III can adsorb R507A as high as 1.3 g/g within an adsorption time interval of 1100 s [46].

4.9. *Activated carbon/n-butane*

The adsorption isotherms of n-butane (C_4H_{10} normal boiling point is -0.55°C) on pitch based activated carbon (Maxsorb III) at temperatures ranging from 25°C to 55°C and at different equilibrium pressures between 20 and 300 kPa have been experimentally measured by a volumetric technique. The isosteric heat of n-butane on Maxsorb III was 406 kJ/kg with a loading of 0.7g/g. The derived monolayer capacity of Maxsorb III-n-butane pair had been measured as 0.8 g/g with an adsorption temperature of 35 °C and 232.34 kPa. The time of adsorption with 25 °C was about 1400 s [47].

4.10. *Activated carbon/CO_2*

An activated carbon in beads form used with CO_2 as an adsorption pair to study experimentally its adsorption equilibria and kinetics. Adsorption equilibrium for CO_2 was measured at different temperatures and pressures. The highest adsorption capacity was 0.0844 g/g at 30 °C and 100 kPa. The isosteric heat magnitude was also determined to be 23.17 kJ/mol [43].

Hines et al. [48], also studied the adsorption characteristics of Maxsorb activated carbon with CO_2. The adsorption capacity was 1.135 g/g at 25 °C and 4586 kPa. The isosteric heat was determined to be 16.2 kJ/mol.

5. Results And Discussion

Figure 2 shows the maximum reached COP for the different adsorption pairs. It is clear from the figure that silica gel and chlorides with water pair has the highest COP value. Zeolite with water pair has the minimum value for COP. From figure 3, it is clear that the lowest value for evaporation temperature is with metal hydrides and hydrogen and this because that the hydrogen has a very low normal boiling point (-252.87 °C). According to the driving temperature figure 4 showed that silica gel and chlorides with methanol pair has the lowest driving temperature. Zeolite and water pair has the highest driving temperature.

Table 2 introduces the characteristics of the reviewed new adsorption pairs. It is clear from the table that there is a new adsorption pairs have a high capacity with a low evaporation temperature. Among these pairs activated carbon with R134a and activated carbon with R50a which have a relatively high adsorption capacity and low evaporation temperature. Activated carbon with diethyl Ether also showed a high adsorption capacity.

Table 2. Characteristics of the new adsorption pairs.

Adsorption pair	**q_{st} kJ/kg**	**C g/g**	**T_{ads} °C**	**P kPa**	**T_b °C**	**t s**
Activated carbon/hydrogen	2800	0.055	30	6000	-252.87	
Zeolite/CO_2	988.64	0.27	0	100	-78.51	
Zeolite/N_2	435.7	0.04	0	100	-195.8	
Activated carbon fibers/N_2	417.9	0.8	-196		-195.8	
Activated carbon/N_2	625	0.00756	30	100	-195.8	
Activated carbon/Diethyl Ether	619.5	1.63	35	10	34.45	1200
Activated carbon/R134a	205.82	2	30	800	-26.55	1200
Activated carbon/R507a		1.3	20		-47.1	1100
Activated carbon/n-butane	406	0.8	25	232.34	-0.55	1400
Activated carbon/CO_2	526.6	0.0844	30	100	-78.51	

6. Conclusion

The study reviewed the adsorption pairs used in cooling applications. A comparison between the working conditions for the already working adsorption cooling system was introduced. Silica gel and chlorides with water pair was had the highest COP value. Zeolite with water pair has the minimum value for COP. The lowest value for evaporation temperature was with metal hydrides and hydrogen. According to the driving temperature, silica gel and chlorides with methanol pair has the lowest driving temperature. Zeolite and water pair has the highest driving temperature.

Also the characteristics of the new adsorption pairs were conducted. Many new pairs show a promising future for cooling application. Finally it is clear from the study that the adsorption cooling is still need for more attention and is still have the opportunity to be a traditional device.

References

Alghoul, M.A., *et al*. (2007). Advances on multi-purpose solar adsorption systems for domestic refrigeration and water heating**,** *Applied Thermal Engineering*,27:813-822.

Al-Ghoutia, Mohammad A., et al.(2010), Characterization of Diethyl Ether Adsorption on Activated Carbon Using a Novel Adsorption Refrigerator**,** *Chemical Engineering Journal Accepted Manuscript.*

Aristov Yu.I., et al. (2002). A family of new working materials for solid sorption air conditioning systems, *Applied Thermal Engineering* 22, : 191-204.

B.,El-Sharkawy B.*et. al*. (2008) . Experimental investigation on activated carbon–ethanol pair for solar powered adsorption cooling applications, *International Journal of Refrigeration* 31: 1407–1413.

Chen, C.J., (2010) . Study on a compact silica gel–water adsorption chiller without vacuum valves: Design and experimental study, *Applied Energy* 87 :2673–2681.

Critoph R.E.and Metcalf, S.J.(2004) Specific cooling power intensification limits in ammonia–carbon adsorption refrigeration systems, *Applied Thermal Engineering*, 24: 661–678.

Critoph, R. E.,(1996). Evaluation of alternative refrigerant-adsorbent pairs for refrigeration cycles, *Applied Thermal Engineering* 16 ,11,pp 891-900.

Duenas C., (2001).Dynamic study of the thermal behavior of solar thermochemical refrigerator: barium chloride-ammonia for ice production, Solar Energy Materials & *Solar Cells* 70 :401–413.

El-Sharkawy, I.I.,*et. al*. (2009) .Study on adsorption of methanol onto carbon based Adsorbents, *International journal of refrigeration* 32: 1579–1586.

Gordeeva Larisa G., *et.al*., (2009).Adsorption properties of composite materials (LiCl + LiBr)/silica, *Microporous and Mesoporous Materials* 126: 262–267.

Grisel Ruud J.H. , Smeding Simon F.and de Boer Robert, (2010) . Waste heat driven silica gel/water adsorption cooling in trigeneration, *Applied Thermal Engineering* 30 :1039–1046.

Habib Khairul, et.al., (2010) .Shigeru Koyama, Kim Choon Ng, Experimental study on adsorption kinetics of activated carbon/R134a and activated carbon/R507A pairs, *International journal of refrigeration* 33: 706–713.

Han Jong Hun and Lee Kun-Hong, (2001) .Gas permeability of expanded graphite-metallic salt Composite, *Applied Thermal Engineering* 21 :453-463.

Hines, A.L., Kuo S.L.and Dural N.H., (1990). A new analytical isotherm equation for adsorption on heterogeneous adsorbents, Sep. *Sci. Technol*. 25, 7-8, pp 869–888.

HU, ERIC J., (1998). A STUDY OF THERMAL DECOMPOSITION OF METHANOL IN SOLAR POWERED ADSORPTION REFRIGERATION SYSTEMS. *Solar Energy* 52, 5, pp 325–329.

Hu Peng, Yao, Juan-Juan and Chen Ze-Shao, (2009). Analysis for composite zeolite/foam aluminum–water mass recovery adsorption refrigeration system driven by engine exhaust heat, *Energy Conversion and Management* 50 : 255–261

Huang Chen-Chia, Chen Hsiu-Mei and Chen, Chien-Hung (2010) .Hydrogen adsorption on modified activated carbon, *International journal of hydrogen energy* 35:2777–2780.

Kato, Y., Sasaki, Y.and Yoshizawa, Y., (2005). Magnesium oxide/water chemical heat pump to enhance energy utilization of a cogeneration system, *Energy* 30 :2144–2155.

Kim, K. J.,*et.al*.,(1997). COMPRESSOR-DRIVEN METAL-HYDRIDE HEAT PUMPS, Applied Thermal Engineering 17, 6 , pp551-560.

Kojima,Y.,et.al., (2006). Hydrogen adsorption and desorption by carbon materials, *Journal of Alloys and Compounds* 421 :204–208.

Kato Y.et.al.(1996) .KINETIC STUDY OF THE HYDRATION OF MAGNESIUM OXIDE FOR A CHEMICAL HEAT PUMP. *Applied Thermal Engineering* 16, 11,pp 853-862.

Lee, Chan Ho, *et.al*. (2005) . Characteristics of non-uniform reaction blocks for chemical heat pump, *Chemical Engineering Science* 60: 1401 – 1409.

Lemmini Fatiha and Errougani Abdelmoussehel, (2007) Technical Note Experimentation of a solar adsorption refrigerator in Morocco, *Renewable Energy* 32 : 2629–2641.

Maggio, G., *et.al*. (2009).Simulation of a solid sorption ice-maker based on the novel composite sorbent ''lithium chloride in silica gel pores", *Applied Thermal Engineering* 29: 1714–1720.

Oliveira. R.G.,Wang, R.Z.and Wang, C.,(2007) .Evaluation of the cooling performance of a consolidated expanded graphite calcium chloride reactive bed for chemisorption icemaker, *International Journal of Refrigeration* 30 :103-112.

Ridha, Firas, N.and Webley, Paul A., (2010). Entropic effects and isosteric heats of nitrogen and carbon dioxide adsorption on chabazite zeolites, *Microporous and Mesoporous Materials* 132:22–30.

Rivera, C., *et.al*. (2007). Experimental study of a thermo-chemical refrigerator using the barium chloride–ammonia reaction, International Journal of Hydrogen Energy 32: 3154 – 3158.

Saha B.B., et.al. (2007). Study on an activated carbon fibereethanol adsorption chiller: Part I e system description and modeling, International Journal of Refrigeration 30: 86-95.

Saha, B.B., et.al. (2007). Study on an activated carbon fiber ethanol adsorption chiller: Part IIe performance evaluation, *International Journal of Refrigeration* 30: 96-102.

Sakintuna, Billur, Lamari-Darkrim, Farida and Hirscher, Michael, (2007). Metal hydride materials for solid hydrogen storage:Areview, *International Journal of Hydrogen Energy* 32: 1121–1140.

Saha, Bidyut B., et.al., (2009) .Adsorption characteristics and heat of adsorption measurements of R-134a on activated, International journal of refrigeration 32:1563–1569.

Saha, Bidyut Baran, *et.al.*, (2008) .Isotherms and thermodynamics for the adsorption of n-butane on pitch based activated carbon, *International Journal of Heat and Mass Transfer* 51: 1582–1589.

Shen, Chunzhi, *et.al*. (2010) .Adsorption equilibria and kinetics of CO2 and N2 on activated carbon beads, *Chemical Engineering Journal* 160: 398–407.

Solmus, Ismail, *et.al*. (2010) .Adsorption properties of a natural zeolite–water pair for use in adsorption cooling cycles, *Applied Energy* 87: 2062–2067.

Srivastava, N.C.and Eames, I.W., (1998) A review of adsorbents and adsorbates in solid-vapour adsorption heat pump systems, *Applied Thermal Engineering* 18 :707-714.

Tamainot-Telto,et.al., (2009) Carbon–ammonia pairs for adsorption refrigeration applications: ice making, air conditioning and heat pumping, *international journal of refrigeration* 32: 1212–1229.

Tamainot-Telto, Z. and Critoph R.E., (1997) Adsorption refrigerator using monolithic carbon-ammonia pair, *International journal of refrigeration* 20, 2, pp 146-155.

Wang, D.C.,*et al.* (2010) A review on adsorption refrigeration technology and adsorption deterioration in physical adsorption systems, *Renewable and Sustainable Energy Reviews* 14 344–353

Wang, L.W., Wang,R.Z.and Oliveira,R.G., (2009) A review on adsorption working pairs for refrigeration, *Renewable and Sustainable Energy Reviews* 13 :518–534.

Wang, L.W., (2006) **The** performance of two adsorption ice making test units using activated carbon and a carbon composite as adsorbents, *Carbon* 44: 2671–2680.

Wang, D.C., Xia, Z.Z.and Wu, J.Y., (2006) .Design and performance prediction of a novel zeolite–water adsorption air conditioner, *Energy Conversion and Management* 47: 590–610.

Wang, L.W.et.al., (2006) .The performance of two adsorption ice making test units using activated carbon and a carbon composite as adsorbents, *Carbon* 44 :2671–2680.

Wang,*et.al*. (2003). Study of the performance of activated carbon–methanol adsorption systems concerning heat and mass transfer, *Applied Thermal Engineering* 23: 1605–1617.

Willers, E.and Groll, M., (1999). Evaluation of metal hydride machines for heat pumping and cooling applications, *International Journal of Refrigeration* 22:47-58.

Veselovskaya, J.V., Tokarev, M.M. and Aristov, Yu. I., (2010). Novel ammonia sorbents ‘‘porous matrix modified by active salt” for adsorptive heat transformation 1. Barium chloride in various matrices, *Applied Thermal Engineering* 30: 584–589.

Veselovskaya, J.V.*et.al*., (2010) .Novel ammonia sorbents ‘‘porous matrix modified by active salt” for adsorptive heat transformation: 3. Testing of ‘‘BaCl2/vermiculite” composite in a lab-scale adsorption chiller, *Applied Thermal Engineering* 30:1188–1192.

Yang, Cheol-Min and Kaneko, Katsumi, (2002).Adsorption Properties of Iodine-Doped Activated Carbon Fiber, *Journal of Colloid and Interface Science* 246**:** 34–39.

Zhong,Y., Critoph, R.E.,and Thorpe, R., (2006). Evaluation of the performance of solid sorption refrigeration systems using carbon dioxide as refrigerant, *Applied Thermal Engineering* 26:1807–1811.