World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:7, No:11, 2013

Adsorption Refrigeration Working Pairs: The State-of-the-Art in the Application

Ahmed N. Shmroukh, Ahmed Hamza H. Ali, Ali K. Abel-Rahman

Abstract**—**Adsorption refrigeration working pair is a vital and is the main component in the adsorption refrigeration machine. Therefore the development key is laying on the adsorption pair that leads to the improvement of the adsorption refrigeration machine. In this study the state-of-the-art in the application of the adsorption refrigeration working pairs in both classical and modern adsorption pairs are presented, compared and summarized. It is found that the maximum adsorption capacity for the classical working pairs was 0.259kg/kg for activated carbon/methanol and that for the modern working pairs was 2kg/kg for maxsorb III/R-134a. The study concluded that, the performances of the adsorption working pairs of adsorption cooling systems are still need further investigations as well as developing adsorption pairs having higher sorption capacity with low or no impact on environmental, to build compact, efficient, reliable and long life performance adsorption chillier. Also, future researches need to be focused on designing the adsorption system that provide efficient heating and cooling for the adsorbent materials through distributing the adsorbent material over heat exchanger surface, to allow good heat and mass transfer between the adsorbent and the refrigerant.

Keywords**—**Adsorption, Adsorbent/Adsorbate Pairs, Refrigeration.

I. INTRODUCTION

THE increase in people's living standards, leads to an increase in needing of comfortable and suitable homes or working environment, this leads to an increase in the demand for Heating, Ventilation and Air-Conditioning (HVAC) systems. Therefore for the target of clean environment and efficient use of energy, research and development in the field of air conditioning need to have more development for the air conditioning and refrigeration systems to be driven from renewable resources such as solar energy. In such case this may leads to a decrease in the electrical energy demand especially in peak periods. Also, the adverse effect of conventional air conditioning and refrigeration systems on the environment, as they use the traditional refrigerants, which has a significant increase the global worming as well as accelerating depletion of the ozone layer. Thus one of the alternative solutions to the develop refrigeration and air conditioning systems to be efficient in energy use and less environmental impacts such as adsorption based systems.

The concept of adsorption refrigeration is based on the evaporation and condensation of a refrigerant combined with adsorption or chemical reaction. Adsorption refrigeration systems (ARS) uses solid adsorbent beds to adsorb and desorb a refrigerant to obtain cooling effect. The basic adsorption refrigeration system usually consists of four main components: a solid adsorbent bed or adsorber, a condenser, an expansion device and an evaporator [1]. Schematic of the cycle is shown in Fig. 1. The system operates on the principle of the reversible adsorption between the adsorbent and the refrigerant, this reversibility depends on the adsorbent temperature and the vapor pressure of the refrigerant. To obtain a continuous and stable cooling effect in ARS, generally two or more adsorbers are used. In the two-adsorber cycle (two-bed adsorption), one is heated during the desorption period and the other adsorber is cooled during the adsorption period, then the complete cycle is known as “cycle time”. The heating and cooling periods are reversed when the adsorbers reach the desired upper and lower temperature limits of the refrigeration cycle, which depend on the selection of the refrigerant fluid and the adsorbent [2]. Recently there is more interest in development of adsorption refrigeration technology for different reasons. Among of them, the sorption systems are quiet, long lasting, cheap to maintain and environmentally benign [3]. The adsorption cooling and refrigeration systems have the advantages of being, free or nearly free of moving parts, efficiently driven by low-temperature waste heat or renewable energy sources, and do not require any synthetic lubricants [4].

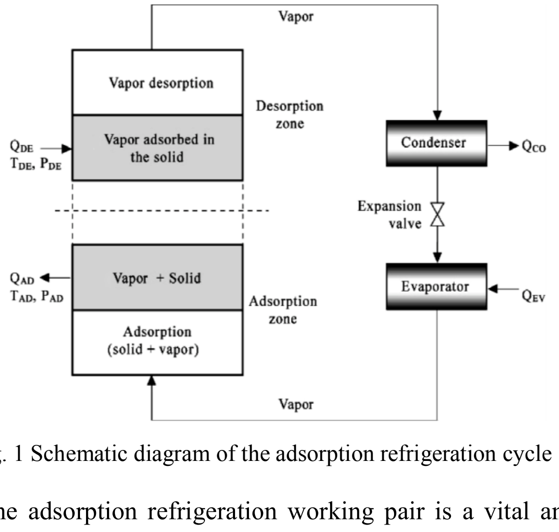

Fig. 1 Schematic diagram of the adsorption refrigeration cycle [2]

The adsorption refrigeration working pair is a vital and is the main component in the adsorption refrigeration machine. Therefore the development key is laying on the adsorption pair that leads to the improvement of the adsorption refrigeration machine. A wide variety of working pairs are possible

Ahmed N. Shmroukh is a PhD student (ahmed.shmroukh@ejust.edu.eg), Ahmed Hamza H. Ali is a professor (ahmed.hamza@ejust.edu.eg) of Refrigeration and Air Conditioning and chairperson of the Department of Energy Resources Engineering and Ali K. Abel-Rahman is a professor. All authors affiliated to Egypt- Japan University of Science and Technology E-JUST, New Borg Elarab, Alexandria 21934, Egypt.

solutions for application in adsorption chillers [5]. Most working pairs use water as the refrigerant due to the highest evaporation enthalpy of water compared to other possible working fluids. Furthermore, water is not toxic and easy to handle. The disadvantage of water is its limitation to applications above 0°C. For ice making or refrigeration below 0°C, methanol or ammonia as refrigerant is used with a variety of solid adsorbents with the main focus on the absorber material from activated carbons [5].

The scope of this paper is to present the state-of-the-art in the application of the adsorption refrigeration working pairs in both classical and modern adsorption pairs. This will be done through the latest review of the published literature in both theoretical and experimental works with working pairs. This is to clarify the state of art of the most efficient and suitable pairs to be used in the ARS applications. However, due to the large number of the published work in open literature on adsorption systems and their pairs, most of the available data in the literature for different working pairs are summarized in this work and a comparison between them are done and their applicability to be used in adsorption refrigeration applications are presented.

II. STATE OF ART OF ADSORPTION PAIRS

A. Classical Working Pairs

Classical working pairs are zeolite/water, silica-gel/water and activated-carbon/methanol as reported in [5]. The available published work with the adsorption data related to the classical working pairs and the adsorption data of these classical pairs will be presented briefly and summarized at the end of this study.

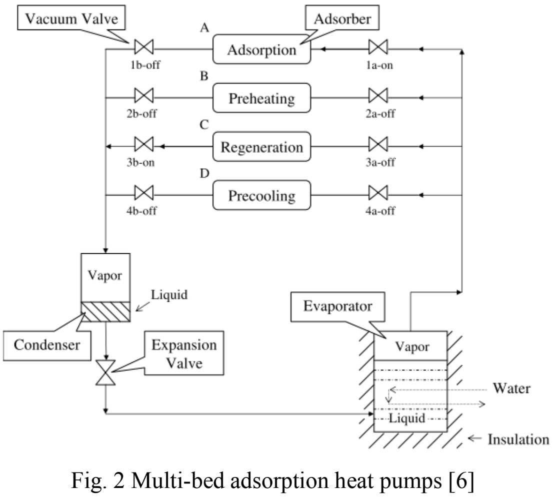

Fig. 2 Multi-bed adsorption heat pumps [6]

San et al. [6] carried out a comparison among the three classical adsorption pairs for using as the working substances in a multi-bed adsorption heat pump. These pairs were activated carbon–methanol, silica gel–water and zeolite 13X molecular sieves–water. Schematic of their test rig is indicated in Fig. 2. The multi-bed adsorption heat pump system they used was contained seven basic components, including four adsorbers, one evaporator, one condenser and one expansion valve. During a cyclic operation, the adsorbers consecutively and orderly proceed to four different modes which were adsorption; preheating, regeneration and precooling as shown in their system (see Fig. 2). In case the adsorber (A) is in the adsorption mode, adsorbers (B), (C) and (D) would be in the preheating, regeneration and precooling modes, respectively. While adsorber (A) switches from the adsorption mode to the preheating mode, adsorbers (B), (C) and (D) would switch to the regeneration, precooling and adsorption modes, respectively. After adsorber (A) accomplishes the four modes, the system proceeds to the next cycle. At this time, adsorber (A) will return to the adsorption mode. Similarly, adsorbers (B), (C) and (D) would return to the preheating, regeneration and precooling modes, respectively. During the precooling or adsorption period, a cold stream of water passes through the base of the insert to cool the adsorbent in the adsorber, during the preheating or regeneration period, through valve control the cold stream is replaced by a hot stream for heating the adsorbent. Their results showed that small mass flow rates of the heating/cooling fluid, assuming a constant temperature for the heating/cooling fluid might give rise to an over-predication of the system performance. Also for adsorption temperature of 30°C, the maximum possible adsorbate contents in adsorbent were, 0.259kg of adsorbate/kg of adsorbent at 5230 Pa for activated carbon–methanol pair, 0.116kg of adsorbate/kg of adsorbent at 958.7 Pa for silica gel–water pair and 0.236kg of adsorbate/kg of adsorbent at 958.7 Pa for 13X molecular sieves–water pair. From the work of San et al. [6] it is noted that, this system need very low operating pressure in case of dealing with water as adsorbent pair.

B. Modern Working Pairs

There are many modern working pairs were found in the open literature. The available published work with the adsorption data related to the modern working pairs and the adsorption data of these modern working pairs will be presented and summarized at the end of this study.

1. Review Studies

Askalany et al. [7] presented a review on adsorption cooling systems with adsorbent pairs of activated carbon with ammonia, methanol, ethanol, hydrogen, nitrogen and diethyl ether pitch based activated carbon (Maxsorb III) with R134a, R507A and n-butane and activated carbon/CO_2 respectively. Their review showed that the highest adsorption capacity for activated carbon/hydrogen pair was 0.055g/g at 30°C and 6 bar, for activated carbon fibers/nitrogen pair was 0.75g/g at -4 °C, for activated carbon / diethyl ether pair was 0.00139g/g at 50°C and 0.1 bar, for activated carbon /R134a pair was 2g/g at 30°C and 8 bar, for activated carbon /R507a pair was 1.3g/g at 20°C, for activated carbon /n-butane pair was 0.8 g/g at 35°C and 2.3 bar and for activated carbon / CO_2 pair was 0.084g/g at 30°C and 1 bar respectively. They also concluded that the maximum COP of the cooling systems was 0.8 for activated carbon/ethanol pair and the performances of the potential adsorption cooling systems using carbon are still not satisfied.

From this work it is can be noted that the refrigerants R134a and R507a have high global warming potential (GWP), also n-butane, hydrogen, methanol, ethanol and diethyl ether are highly flammable gases and ammonia is a highly toxic refrigerant. Aristov [8] presented review of many porous solids offered by material science which may be used for adsorption transformation of low temperature heat. He also gave an overview of original and literature data on several classes of those materials, such as metalaluminophosphates (which represent the first family of framework oxides synthesized without silica), porous coordination polymers (which are new family of super molecular materials, also called metal-organic frameworks) and salt in porous matrix composite sorbents (as LiCl/silica, $BaCl_2$/vermiculite). His data showed that FAM-Z02 (silicoaluminophosphate) exchange large amount of water (up to 0.2g/g) within narrow temperature and humidity ranges. The amount of methanol and water adsorbed by porous coordination polymer reaches 0.19g/g and 0.21g/g, respectively. Composite sorbent of methanol in LiCl/silica can adsorb up to 0.6g of methanol per 1g of dry sorbent at 30°C and new sorbent of ammonia $BaCl_2$/vermiculite sorbs 0.25 g/g. He also cited that, an optimal adsorbent should provide a moderate affinity toward sorbate molecules that depends on particular boundary conditions of the cycle. From this work, it can be noted that methanol is a combustible and toxic gas and ammonia is highly toxic gas. Askalany et al. [9] presented an overview on adsorption pairs used in cooling applications. These pairs include, Activated carbon /ammonia, Activated carbon /ethanol, Metal hydrides/Hydrogen, expanded graphite calcium chloride/ammonia, composite zeolite and foam aluminum/water, Zeolite/N_2, Activated carbon/N_2. Their survey demonstrates that the maximum adsorption capacity for Activated carbon /ammonia pair was 0.29g/g, for Activated carbon /ethanol pair was 1.2g/g, for Metal hydrides/Hydrogen pair was 0.073g/g at 0.6 bar, for expanded graphite calcium chloride/ammonia composite pair was 0.239kg/kg, for composite zeolite and foam aluminum/water pair was 0.22 g/g, for Zeolite/N_2 pair was 0.04g/g at 10°C and 100 kPa and for Activated carbon/N_2 pair was 0.00756g/g at 30°C and 100 kPa. They concluded that the adsorption cooling systems still require significant research and development activities.

2. Theoretical Studies

Zhou et al. [10] investigated theoretically the main thermodynamic parameters for adsorption such as the enthalpy change, the free energy and entropy for adsorption of SO_2, NO and CO_2 from flue gas on activated carbon fiber (ACF) at 70 kpa. Also cited that these parameters could provide useful information elucidated the behavior of adsorption process. The equilibrium data were analyzed by the following Langmuir equation (1) and Freundlich equation (2):

$$W = \frac{w_0\,bp}{1 + bp} \tag{1}$$

$$W = kp^{1/n} \tag{2}$$

where W is the amount adsorbed, p is the equilibrium pressure, w_0 represents the maximum amount adsorbed, b the affinity that depends on temperature, k is Freundlich constants and 1/n is the heterogeneity factor. They revealed that Freundlich model was more suitable to describe the three gases adsorption than Langmuir model. Their results showed that from the Langmuir adsorption equation at 323.15K the maximum adsorption amount of SO_2 was 9.086 mmol/g at 52 kPa, NO was 5.546 mmol/g at 56 kPa and CO_2 was 4.629 mmol/g at 65 kPa. From the work of Zhou et al. [10] clearly that SO_2 and NO are very corrosive and toxic gases. Bhagiyalakshmi et al. [11] investigated theoretically the adsorption, regeneration and interaction of CO_2 with a polythiophene–carbon (PTP–OMC) mesocomposite. Their results showed that at atmospheric pressure, the maximum adsorption capacity of PTP–OMC–II was 125mgCO_2/g at 25°C and 120mgCO_2/g at 25°C for PTP–OMC–I. From the work of [11] it can be noted that the adsorbent PTP–OMC –I and II have a very low adsorption capacity. Jribi et al. [12] investigated theoretically the thermodynamic analysis of activated carbon-CO_2 based adsorption cooling cycles, using the pressure-temperature-concentration (P-T-W) diagram. This diagram is used to describe the thermodynamic relation between the equilibrium pressure, adsorption temperature and amount of refrigerant adsorbed per unit mass of adsorbent. They also provide a simple prediction of the performances of the ideal adsorption cooling cycle. In their study, the driving heat source temperatures was ranged from 30°C to 90°C at different cooling load temperatures with a heat sink temperature of 25°C. In their analysis, they used Tóth isotherm equation (3) to calculate the amount of CO_2 adsorbed on to Maxsorb (pitch-based activated carbon powder) and A10 activated carbon (a type of activated carbon fiber) as a function of pressure and temperature.

$$W = \frac{w_0\,bp}{\left(1 + (bp)^n\right)^{1/n}} \tag{3}$$

where W is the amount adsorbed, p is the equilibrium pressure, w_0 represents the saturated amount adsorbed, b the affinity that depends on temperature, and n is the heterogeneity factor. They found that Maxsorb contains about 3 times higher CO_2 uptake comparing to A10. Moreover, their results showed that the coefficient of performance (COP) of adsorption cycle incorporating Maxsorb activated carbon as adsorbents is 0.15, which is higher than that of the case of A10 activated carbon based adsorption system which is 0.083. This proposed adsorption system seems to be suitable for automobile air-conditioning and heat pumping applications. From this study, it can be noted that CO_2 has a bad effect on central nervous system in the case of high concentration leakage from adsorption refrigeration systems. Hai-jun et al. [13] prepared a series of attapulgite (AT)-based Lithium Chloride LiCl composites with mixing method, for cooling and air conditioning applications. Their results showed that at 1500 Pa and 30°C water loading (adsorbate) on AT–LiCl (30%) the adsorption capacity can be as high as 0.44kg/kg, which was higher than commonly used zeolite 13X and silica gel. Also they cited that attapulgite clay has an ideal water loading of about 0.20kg/kg as well as good containing ability for water due to its highly porous structures. However, it should be considered from their work that water adsorbate based refrigeration systems need very low operating pressure to prevent icing. Carvalho et al. [14] evaluated the adsorption of a recalcitrant fluoroaromatic compound, fluorobenzene (FB), onto Granular Activated Carbon (GAC). They cited that halogenated aromatic compounds were important environmental pollutants of soil, water and air. Fluorinated compounds as fluorobenzene (FB) is categorizes as halogenated aromatic compounds, were used due to their useful applications, such as refrigerants. They monitored and investigated the adsorption of FB to the GAC experimentally, then they fitted the experimental data with the Langmuir, Freundlich and Redlich–Peterson (4).

$$W = \frac{c w_0}{1 + a w_0^d} \tag{4}$$

where W is the amount adsorbed, w_0 is the saturated amount adsorbed, c and a are the Redlich–Peterson isotherm constants and d is the Redlich–Peterson isotherm exponent, which lies between 0 and 1 models.Their results showed that respective fitted isotherms of Redlich–Peterson model giving the best fitting, Freundlich model also provided a good fit but the Langmuir model could not adequately fit the experimental data, especially at high FB concentrations. Also they found that at 25°C the maximum adsorption capacity of FB onto GAC was found to be 388mg of FB per gram of GAC. It should be noted from the work of [14] that fluorobenzene is flammable and toxic gas. Solmus et al. [15] provided a numerical investigation of coupled heat and mass transfer inside the adsorbent bed of a silica gel/water adsorption cooling unit, using the local volume averaging method. They developed a transient one-dimensional local thermal non-equilibrium model, which accounts for both internal and external mass transfer resistances. Their adsorption bed is shown in Fig. 3. The model was based on the following assumptions and simplifications: the size of the adsorbent particles and the bed porosity were spatially uniform; the adsorbate's vapor phase was assumed to be an ideal gas; radiative heat transfer, viscous dissipation and the work done by pressure changes were neglected; the surface porosity was considered to be equal to the total porosity; physical properties such as thermal conductivities, specific heat capacities and viscosity were not a function of temperature; the wall thickness of the vacuum tube is assumed to be very thin and hence, its thermal resistance was neglected. Their results showed the significant of spatial temperature and pressure gradients clearly indicate that heat transfer and external mass transfer resistance are important. While significant deviations of the amount adsorbed from the equilibrium amount adsorbed indicate that internal mass transfer resistances are also important. They concluded that to improve the performance of the bed, efforts should be focused on reducing heat transfer resistances and intra-particle (interior) mass transfer resistances but not inter-particle (exterior) mass transfer resistances. Cui et al. [16] performed a study on the performance of environmentally benign working pairs for adsorption refrigeration. Water and ethanol were selected as refrigerants while NA and NB were the targeted adsorbents, they did not mention any information about the composition of these adsorbents. They cited that this new composite adsorbent, NA and NB, has been developed by the authors and can be regenerated at relatively lower temperature and can keep large adsorption capacity even at low aqueous partial pressure. Their results showed that, at 27°C the maximum adsorption capacity of water on proposed NA reaches 0.7 kg/kg, which is 2.3 times that of water on zeolite 13X. The maximum adsorption capacity of ethanol on NB is 0.68 kg/kg, which is three times that of ethanol on activated carbon. Thus these environmental friendly and no public hazard adsorption working pairs, NA–H_2O and NB–ethanol can substitute activated carbon–methanol in adsorption refrigeration system using low-grade heat source. From the work of Cui et al. [16], it is counted that there is no evidence to synthesize these materials in open literature. Tanada et al. [17] provided a study on the adsorption properties of CFC and CFC replacements on activated carbon plasma treated. The CFC and CFC replacements used in their study were chloro-1,2,2-trifluoroethane (R-113), 1,1-dichloro-1-fluoro-ethane (R-141b), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (R-225cb) and 2,2,3,3,3-pentafluoro-1-propanol (5FP). They applied the Dubinin–Radushkevich (DR) (5) to their homogeneous micropores system to describe the physical adsorption behavior of their adsorption pairs.

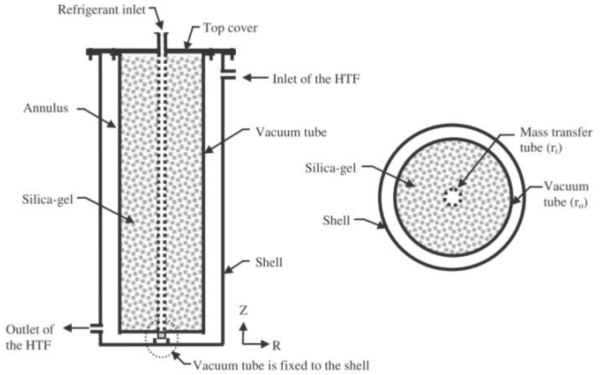

Fig. 3 Schematic view of the cylindrical adsorbent bed [15]

$$W = w_0 \, e^{-\left(\frac{A}{bE_0}\right)^2} \tag{5}$$

$$A = RT \ln\left(\frac{p_0}{p}\right) \tag{6}$$

where W is the amount adsorbed, w_o is the saturated amount adsorbed, T is the absolute temperature, P is the equilibrium pressure, P_o is the saturated pressure, A is the free energy of adsorption, b is the affinity coefficient, and E_o is the characteristic energy of adsorption.

Their results showed that the maximum adsorption capacity of R-113 onto activated carbon was found to be 850 mg/g at 0.5333 bar, R-141b onto activated carbon was found to be 660 mg/g at 0.9333 bar, 5FP onto activated carbon was found to be 880 mg/g at 0.0666 bar and R-225cb onto activated carbon was found to be 860 mg/g at 0.4 bar. From this work it is remarked that all adsorbents used have high global warming potential (GWP) and ozone depletion potential (ODP).

3. Experimental Work

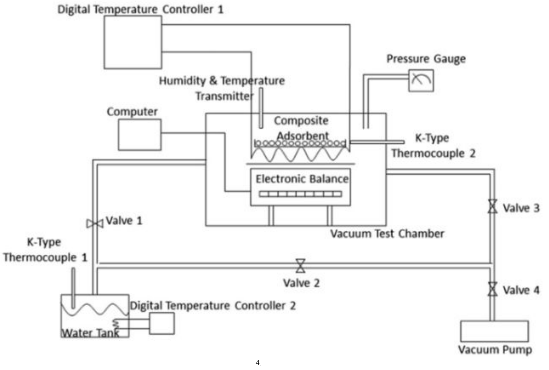

Fig. 4 Schematic diagram of the adsorption test unit [18]

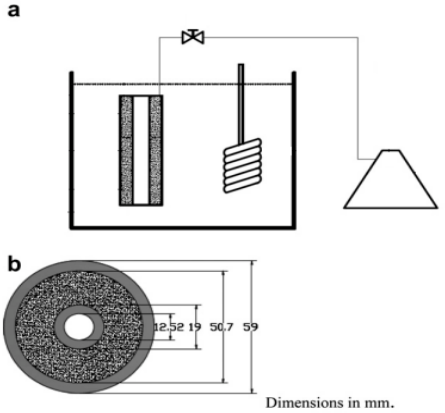

Fig. 5 (a) Schematic diagram of the experimental test rig (b) Cross-section in the adsorption cylinder [21]

Tso et al. [18] carried out a study on composite adsorbents that synthesized from activated carbon, silica-gel and $CaCl_2$, used for energy efficient solar adsorption cooling and dehumidification systems. Thirteen combinations of these three materials were tested to optimize the adsorption characteristics for adsorption cooling and dehumidification system applications. They used an adsorption rate test unit that shown in Fig. 4 to study the adsorption capacities and adsorption rates of the various composites, using the silica activated carbon/$CaCl_2$. Their system had two main components, a water bath evaporator and a test vacuum chamber. The sample adsorbents inside the vacuum chamber were kept at a constant temperature by a digital temperature controller and the adsorption isotherms and adsorption rate curves were recorded at a constant temperature. The silica and $CaCl_2$ had been taken and impregnated into the micropores and mesopores of the raw activated carbon. Their results showed that the maximum adsorption capacity of the activated carbon-silica gel-$CaCl_2$ composite adsorbent was 0.23kg water/ kg adsorbent, as recorded at 27°C and a water vapor pressure of 900 Pa. The maximum adsorption capacity of the raw activated carbon was 0.02kg water/ kg adsorbent at the same conditions. With this combination they improved the adsorption characteristics of the raw activated carbon. They cited that the maximum adsorption capacity of zeolite 13X/$CaCl_2$ composite adsorbent was 0.404kg water /kg adsorbent at 25°C and 870 Pa. Also their experiments showed that $CaCl_2$ could adsorb approximately 0.9g of water vapor per gram of $CaCl_2$ at room temperature and pressure. That is why $CaCl_2$ is one of the adsorbents used widely in dehumidifier boxes. From the results of Tso et al. [18] it is noted that activated carbon has a very low adsorption capacity to water. Also the tested composite adsorbents have lower adsorption capacity than single adsorbent $CaCl_2$. Xin Li et al. [19] studied the adsorption of CO_2 on heterostructure TiO_2 nanotubes (TNTs). Their results showed that he amounts adsorbed of CO_2 on TNTs are 0.269 mmol/g at 1atm pressure and 298K, which was much lower than those of CO_2 in metal-organic framework (MOF-5) which was 92.4mg/g at 1.0 bar and 296K [20], CO_2 in zeolitic imidazole frameworks (ZIF09) which was 209.8mg/g at 273K and 1 bar as of [20] and CO_2 in zeolite13X which was 1.77 mmol/g at 298K and 1 bar. From the data of Xin Li et al. [19], it is cleared that the tested and studied pairs are not sufficient to be used in adsorption refrigeration systems due to their low adsorption capacity. Askalany et al. [21] carried an experimental study on adsorption-desorption characteristics of granular activated carbon/R134a pair, their experimental test rig is illustrated in Fig. 5. All over their experimental runs the temperature of the pairs was kept about 25ºC. Their experimental results showed that increasing the temperature of the adsorbent leads to a decrease on the maximum adsorption capacity until reaches to $0.53kg_{R134a}/kg_{carbon}$ at 60°C for a period of 450s. The maximum adsorption capacity was found to be $1.68kg_{R134a}/kg_{carbon}$ at 25°C after 1000s. Also Askalany et al. [21] concluded that the granular activated carbon and R134a could be used as adsorption pair in an adsorption cooling system. On the other hand depending on the work of [21], it is remarked that R134a has a negative impact on the environmental due to its high GWP. Baiju et al. [22] investigated experimentally the performance of a two stage solar adsorption refrigeration system with activated carbon-methanol pair. That system utilizes a common evaporator placed inside a refrigerator box, a condenser, an expansion device (capillary tube), parabolic solar concentrator, two adsorbent beds and two water tanks as shown in Fig. 6.The system has been designed for heating of 50 liters of water from 25°C to 90°C as well as cooling of 10 liters of water from 30°C to 10°C within one hour. Their results showed that the system has better performance during night time as compared to the day time. The system has a mean cycle COP of 0.196 during day time and 0.335 for night time. The specific cooling power (SCP) indicates the size of the system as it measures the cooling output per unit mass of adsorbent per cycle time, higher SCP values indicate the compactness of the system. The reported that specific cooling power (SCP) means value during day time and night time are 47.83 and 68.2, respectively. The experimental results also demonstrated that the refrigerator has cooling capacity of 47 to 78W during day time and 57.6 to 104.4W during night time. From the work of Baiju et al. [22] it is noted that methanol is a flammable gas and has negative effect on global warming. Glaznev et al. [23] introduced a study on composite adsorbents were synthesized from a meso-structured silicate (SBA-15) and $CaCl_2$, for adsorptive transformation of low temperature heat. The equilibrium and dynamics of water sorption have been studied under typical conditions of isobaric stages of adsorptive heat transformation cycle. Also they made an analysis of the pore size effect on the water sorption properties of composites $CaCl_2$/ SBA-15 applied to adsorptive heat transformation cycles. They synthesized expanded SBA-matrices with the pores of 8.1 and 11.8nm diameters. They reported that the composites with smaller pores were able to generate cold rejecting the adsorption heat to hotter environment, which is a case of the rejection conditions in tracks and passenger cars. Also their results showed that, the maximum adsorption capacity of the SBA-15 with $CaCl_2$ composite adsorbent was $0.7kg_{water}/ kg_{adsorbent}$, measured at temperature 50°C. Bao et al. [24] investigated the performances of different working pairs operating indesorption cycle. Those pairs were also studied gravimetrically by comparing the desorbed and adsorbed mass of refrigerant in different operating conditions. All pairs used NH_3 as refrigerant and $MnCl_2$ in the main reactor, but each one used a different salt for the cooling effect production in the secondary reactor. These salts were NH_4Cl and NaBr. Their results showed that at 30°C the maximum mass of refrigerant (NH_3) that reacted during a cycle was 0.747 g/gadsorbent in the system that used NH_4Cl-$MnCl_2$ composite adsorbent and 0.649g/gadsorbent in the system with NaBr-$MnCl_2$ composite adsorbent. Also they found that, the coefficient of performance (COP) of the system using NH_4Cl and the system using NaBr were similar and around 0.30. However the former system had a specific cooling power (SCP) of 5% higher than that of the latter system. From the work of [24] it should be considered that NH_3 is a very toxic gas. Lithoxoos et al. [25] carried out an experimental work on the adsorption capacity of single-wall carbon nanotubes (SWCNTs) bundles with regard to the pure H_2, CH_4, N_2, CO and CO_2 gases at 298K. Langmuir type equation was adopted to estimate their total adsorption isotherm. Their experimental results showed that the maximum adsorption capacity at 25°C was found to be $0.065kg_{H2}/kg_{SWCNT}$ at 1.92MPa, $0.021kg_{CH4}/kg_{SWCNT}$ at 2.1MPa, $0.019kg_{N2}/kg_{SWCNT}$ at 1.92MPa, $0.042kg_{CO}/kg_{SWCNT}$ at 2MPa and $0.1042kg_{CO2}/kg_{SWCNT}$ at 1.98 MPa. Al-Ghouti et al. [26] built a diethyl ether-activated carbon adsorption refrigerator that shown in Fig. 7. The system is equipped with meshed multi-tubular involving activated carbon in a sealed cylindrical adsorber, which was made up of 19 fined tubes to enlarge the heat transfer surface. Every fined tube in the sealed cylindrical adsorber is filled with the activated carbon and the mass of the activated carbon per bed is 7.8–8.4g. Their system was designed in order to remove the limitations originating from inefficient heat and mass transfer in adsorption refrigeration/heat pump and to characterize the adsorption behavior of that pair. Their results showed that the maximum adsorption amount of the diethyl ether onto the activated carbon was 2.0028mg/g at 35°C and 0.305atm. From the work of [26] it can be noted that, diethyl ether is highly flammable gas. Liu et al. [27] presented an experimental study on a design for a continuous silica gel–water adsorption chiller (with no refrigerant valves), using low temperature heat source ranging from 70 to 85°C. Plate-fin heat exchanger is used in their system to enhance the heat and mass transfer on adsorbers as shown in Fig. 8. In the conventional systems, large diameter vacuum valves in the refrigerant circuit are used when water or methanol is used as refrigerant, no refrigerant valves were provided in this system. Therefore the problem of leakage and pressure drop along the vapor channel can be absolutely avoided as can be seen in Fig. 8. Their system is rather different from that in the conventional system as in the conventional system the mass recovery process is realized through opening of the refrigerant valve connecting the two adsorbers. While in their system, the mass recovery-like process is realized by circulating chilled water between the two evaporators through switching water valves in the chilled water circuit. The second is the drive for mass recovery in a conventional system is pressure difference between the two adsorbers, while in their system it is the temperature difference in the two evaporators. The mass recovery-like process in this system is necessary because, in the heat recovery process, there is an amount of adsorbate adsorbed by adsorber B, but there is no cooling effect output and the cooling effect is mainly used to lower temperature in evaporator B. This process diminishes the effective adsorption capacity in the cycle. The mass recovery-like process can compensate for the amount of adsorbate lost in the heat recovery process.

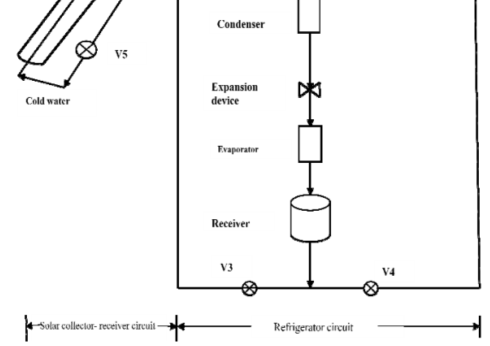

Fig. 6 Schematic diagram of two stage solar adsorption refrigeration system [22]

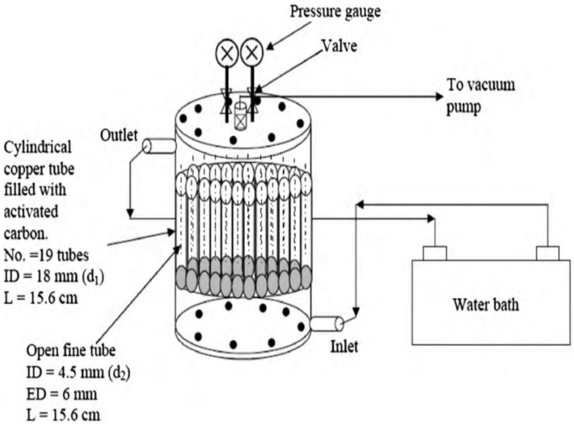

Fig. 7 The adsorption system used in [26]

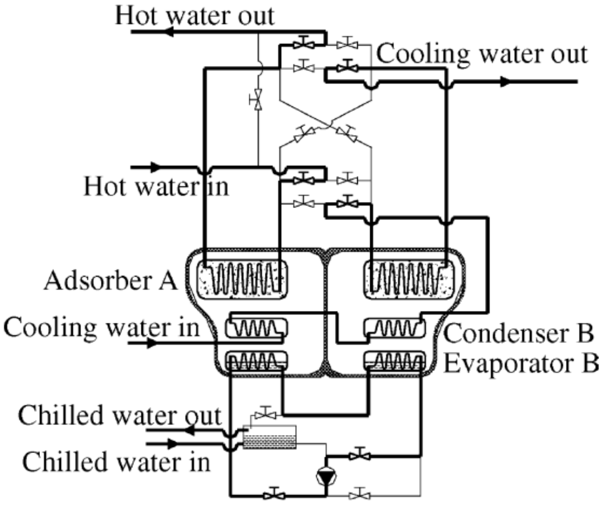

Fig. 8 The mass recovery-like process of [27]

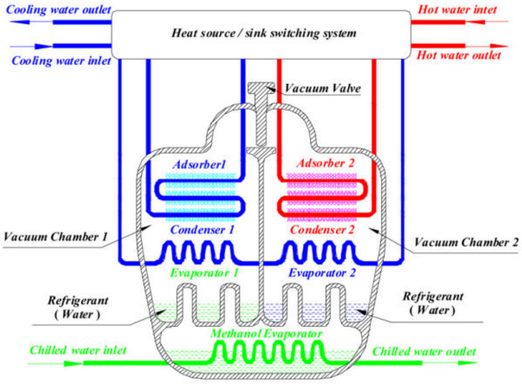

Fig. 9 Schematic diagram of the adsorption chiller of [28]

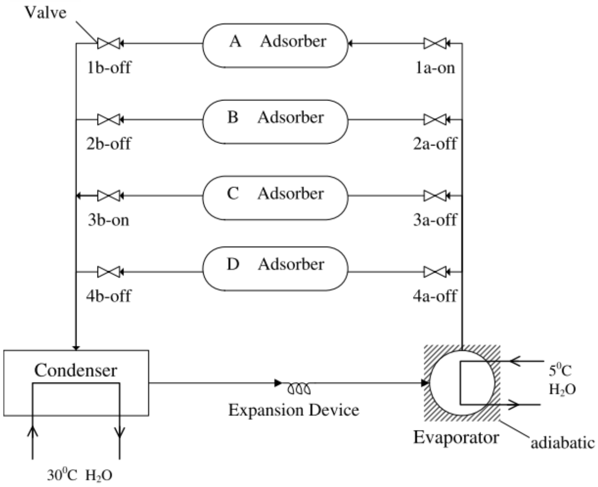

Fig. 10 The multi-bed adsorption heat pump of [29]

Their results showed that the chiller with refrigerant valves has a cooling capacity of 2–7.3 kW and COP ranging 0.2–0.42 according to different evaporating temperatures. However the system chiller performance has been greatly improved, with a heat source temperature of 80°C, a COP over 0.5 and cooling capacity of 9 kW has been achieved at evaporating temperature of 13°C. Xia et al. [28] built a silica gel–water adsorption chiller (driven by hot water of 60–90°C) with three chambers as shown in Fig. 9. The chiller has one condenser, one adsorber and one evaporator that were housed in one vacuum chamber to form an adsorption/desorption unit. For the two vacuum chambers and one methanol evaporator, the cooling power is transferred from one water evaporator into the methanol evaporator via the gravitation heat pipe loop and finally taken away by the chilled water passing through the methanol evaporator. Their results showed that the cooling power and COP of the chiller are 8.70 kW and 0.39 for the heat source temperature of 82.5°C, cooling water temperature of 30.4°C and chilled water outlet temperature of 12°C. For a higher chilled water outlet temperature of about 16°C, the COP increases to 0.43 while the cooling power is about 11.0 kW. Compared with that of the former chiller of [26], the COP of this chiller increases by 20%. San et al. [29] investigated the performances of a multi-bed adsorption heat pump using SWS-1L (silica gel + $CaCl_2$) composite adsorbent and water as the working pair, substitute a regular-density silica gel in the adsorbers. Their proposed four-bed adsorption heat pump test rig can be seen in Fig. 10. It is consisted of seven basic components, including four adsorbers, one evaporator, one condenser and one expansion device. Their results showed that at 30°C as adsorption temperature, the maximum possible adsorption capacity for the SWS-1L composite adsorbent in adsorption of water vapor was 0.275 $kg_{H2O}/kg_{SWS\text{-}1L}$.Also they found that when using the composite adsorbent, the coefficient of performance and the specific cooling power could be increased by 51% and 38.4% respectively, compared when using the regular density silica gel in the four adsorbers. Wang et al. [30] have conducted a study on the adsorption characteristics of the adsorption refrigeration working pairs, using alkaline-earth metal chlorides ($MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$) as adsorbents and ammonia as refrigerant. Their refrigeration system is shown in Fig. 11 and consists of an adsorber, an evaporator/condenser, a constant temperature water bath, connecting pipeline and affiliated parts. The refrigeration capacity of selected adsorbents was tested at different desorption temperature. The adsorption refrigeration cycle includes two processes, adsorption refrigeration process and heating desorption process thus at low temperatures, adsorbent adsorbs refrigerant located in the evaporator. Liquid refrigerant evaporates in the evaporator and was adsorbed in the adsorber. This process adsorbs heat from the refrigeration box, thus the refrigeration occurs. The refrigeration process ended when the adsorbent is saturated. The adsorber which is rich with adsorbed refrigerant is heated with water bath at a set temperature. When the system pressure increases to condensation pressure, the desorbed refrigerant gas condenses in the condenser. Then the next adsorption refrigeration cycle begins. Their results showed that the maximum adsorption capacity of $NH_3/MgCl_2$ pair is $0.38g_{NH3}/(g_{MgCl2})$ at 35°C and 0.2MPa,$NH_3/CaCl_2$ pair is $0.97g_{NH3}/(g_{CaCl2})$ at 35°C and 0.4 MPa,$NH_3/SrCl_2$ pair is $0.87g_{NH3}/(g_{SrCl2})$ at 35°C and 0.25MPa and $NH_3/BaCl_2$ pair is $0.18g_{NH3}/(g_{BaCl2})$ at 35°C and 0.15 MPa.

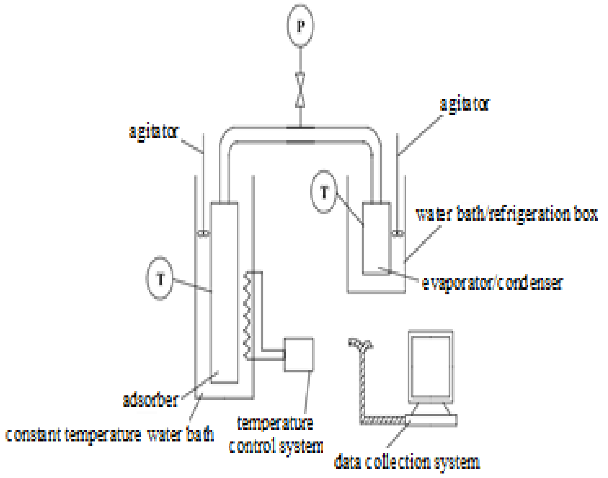

Fig. 11 Scheme of the experimental refrigeration unit proposed by [30]

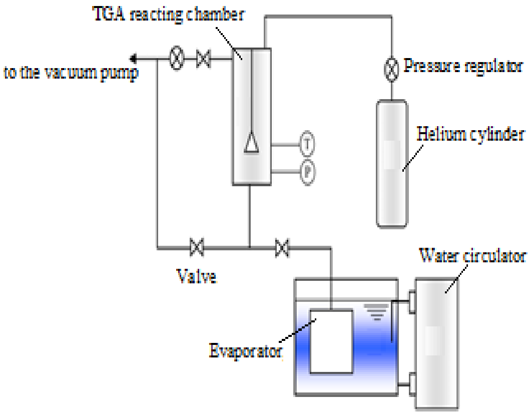

Fig. 12 Schematic diagram of the experimental set up [31]

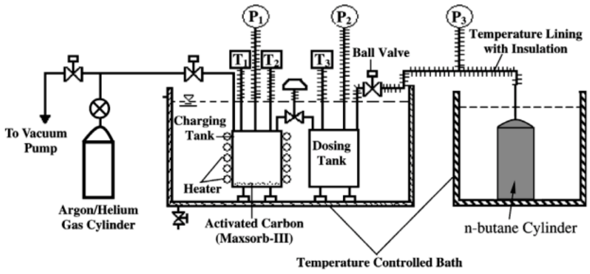

Fig. 13 Schematic diagram of the constant volume variable pressure test facility [32]

From the work of [30] it can be noted that the adsorbent $CaCl_2$ which used NH_3, has higher adsorption capacity than the other tested adsorbents. El-Sharkawy et al. [31] carried out an experimental study on adsorption equilibrium uptake of ethanol onto a highly porous activated carbon based adsorbent, namely Maxsorb III, for solar powered adsorption cooling systems, using a thermo-gravimetric analyzer (TGA) unit. Their experimental set up is shown in Fig. 12. The Dubinin–Astakhov (D–A) equation has been used to correlate the experimental data. Isosteric heat of adsorption is also estimated by using the Clausius–Clapeyron equation. Their results showed that the Maxsorb III can adsorb up to 1.2 kg of ethanol per kilogram of adsorbent, at 20°C adsorption temperature. It can be noted from the work of [31] that, ethanol is flammable and has bad effects on nervous system in case of high concentration leakage. Saha et al. [32] studied experimentally the thermodynamics and isotherms for the adsorption of n-butane on pitch based activated carbon (type Maxsorb III), at temperatures ranging from 298 to 328K and at different equilibrium pressures between 20 and 300kPa. Their apparatus is shown in Fig. 13. They determined the porous properties such as, the density, surface area, pore size, pore volume along with pore size distribution of Maxsorb III. They used Dubinin–Astakhov (DA) adsorption isotherm model to describe all of the isotherm experimental data. Their results showed that the maximum adsorption capacity of Maxsorb III/n-butane pair was measured to be 0.8 kg/kg at 298.15 K and 232.34 kPa. From the work of [32] it can be noticed that, n-butane is a highly combustible gas. Zhong et al. [33] investigated the equilibrium concentration characteristics of ammonia with a composite adsorbent material ($BaCl_2$ impregnated into a vermiculite matrix). Their experimental apparatus can be seen in Fig. 14. The measured data was used for determining the equilibrium adsorption properties of their target pair. The adsorbent sample was contained in a small basket, which was suspended inside the sealed steel chamber. The chamber was within a jacket, through which heated oil is circulated in order to control the temperature of the vessel and the sample. Their results showed that at 37°C the maximum concentration is about $0.4kg_{ammonia}/kg_{adsorbent}$. Also their thermodynamic model of basic adsorption cycles showed that this adsorption pair could have applications in air-conditioning and the COP could reach up to 0.6. Wang et al. [34] performed a comparison on the adsorption performance of compound adsorbent in a refrigeration cycle with and without mass recovery. The adsorption pair was $CaCl_2$ and activated carbon as a compound adsorbent and ammonia as adsorbate. Their test rig is shown in Fig. 15; their unit used for testing the equilibrium adsorption performance of the different pairs was mainly consists of an adsorber putted in an oil tank and condenser/evaporator was kept in ethanol jacket. The adsorber was heated by an electric heater in desorbing period and cooled by water in circuit during the adsorbing period. The temperature of the evaporator/condenser was controlled by a thermostatic bath. Their results showed that at 30°C adsorption temperature, the cycle's maximum adsorption capacity with mass recovery was 0.78kg/kg, while that of the cycle without mass recovery was only about 0.55kg/kg. Also they found that specific cooling power and coefficient of performance have been improved by 48.6% and 54.5%, respectively, when mass recovery is performed. Tamainot-Telto et al. [35] tested three single module configurations (generators with and without aluminium fins) for rotary regenerative adsorption air conditioning system using monolithic carbon–ammonia in a multiple bed design. The basic single module is shown in Fig. 16. They named MODULAR1-0.0 without any fins. While from the basic module there are two other module configurations as shown in Fig. 17 called MODULAR2-0.125 and MODULAR2-0.3 with external aluminum fins to improve the heat transfer capacity of the module. Each of them consists of two basic single modules with both generator and receiver that fitted with rectangular aluminum fins and the difference only in fin thickness in the two modules. Their results showed that the maximum adsorption capacity at 25°C was found to be 0.3837 kg_{NH3}/kg_{Carbon}.

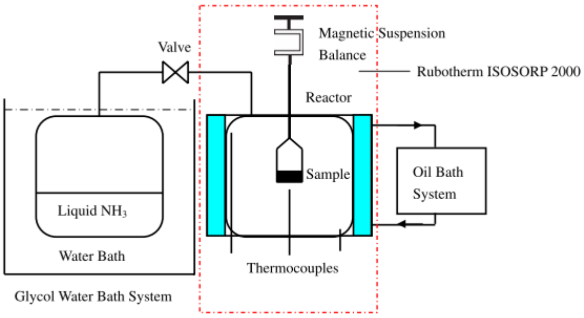

Fig. 14 Schematic diagram of porosity test rig [33]

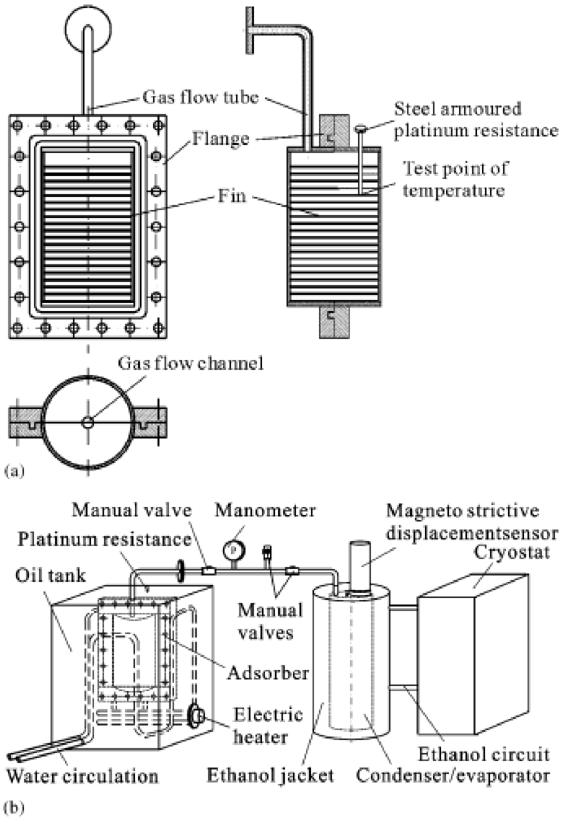

Fig. 15 (a) Structure of adsorber and (b) adsorption system proposed by [34]

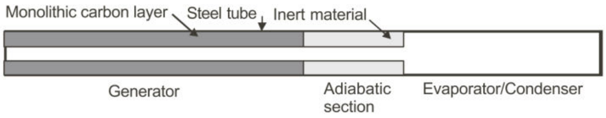

Fig. 16 Schematic diagram of the basic module (MODULAR1-0.0) of [35]

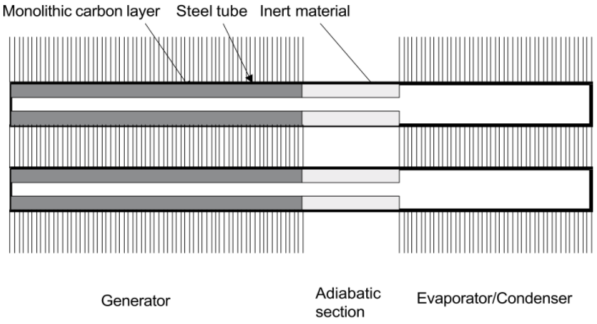

Fig. 17 Schematic diagram of MODULAR2-y type of [35]

Tokarev et al. [36] synthesized and studied a new working material $CaCl_2$ as an impregnated salt confined to a mesoporous silicate (MCM-41) for adsorption cooling/heating applications. For this mesoporous system the isobars, isosters and isotherms of the water sorption are obtained at adsorption temperature of 313K. Their results showed that $CaCl_2$ and MCM-41 composite adsorbent was able to absorb up to 0.75 $kg_{H2O}/kg_{adsorbent}$. Thus this pair could be competitive with the common working materials, like zeolites, silica gels and activated carbons. Moreover, most of water sorbed can be removed at the relatively low temperature between 343 and 393K. This facilitates drastically the usage of heat sources with the low temperature level, like industrial heat wastes, geothermalor solar energy, thus new pair should be considered as a good candidate for the thermal applications driven by the low-temperature heat sources. Their material demonstrates two types of sorption behavior (liquid absorption and solid adsorption) giving an opportunity to combine their advantages. For instance, the solution retention in the solid MCM matrix is likely to allow overcoming the crystallization and corrosion problems that are crucial for liquid absorption units. From the work of [36] it should be considered thatin order to prevent water icing, the adsorption system needed to operate with very low vacuum pressure. Lin et al. [37] conducted an experimental work to investigate gas-phase adsorption characteristics of 1,1-di-chloro-l-fluoroethane (R-141b) by activated carbon fiber (ACF), extruded activated carbon (EAC), granular activated carbon (GAC), activated alumina and molecular sieve. At the beginning of their adsorption experiments, they treated all activated carbon adsorbents (GAC, EAC and ACF) to remove all impurities which might have been adsorbed on the pore surfaces. They reported that the desorption process was performed to regenerate the exhausted adsorbents for reuse. Their results showed that at 25°C the maximum adsorption capacity of R-141b onto ACF was found to be 690mg per gram of ACF, R-141b onto EAC was found to be 620mg per gram of EAC, R-141b onto GAC was found to be 560mg per gram of GAC, R-141b onto activated alumina was found to be 400mg per gram of activated alumina and R-141b onto molecular sieve was found to be 385mg per gram of molecular sieve. From the work of [37] it can be noted that, R-141b has negative effect on the environment due to its high GWP and high ODP. Mariwala et al. [38] presented and obtained the adsorption isotherms of 16 halocarbons on a nanoporous carbon molecular sieve Carbosieve G (CSG). All their adsorption isotherm measurements have been done at 295K in the range of absolute pressures from 0.0661 to 101.3 kPa, and were conducted gravimetrically using a microbalance unit. Their results showed that at 295K as adsorption temperature and 93.33kPa, the maximum possible adsorption capacity for the nanoporous carbon molecular sieve Carbosieve G (CSG) adsorbent in adsorption of R-11 (CCl_3F) was 0.735 kg/kg_{CSG}, for R-12(CCl_2F_2) was 0.644 kg/kg_{CSG}, forR-13 ($CClF_3$) was 0.492kg/kg_{CSG}, forR-21 (CCl_2FH) was 0.669kg/kg_{CSG}, forR-22($CClF_2H$) was 0.57kg/kg_{CSG}, for R-23 (CF_3H) was 0.409kg/kg_{CSG}, forR-30 (CCl_2H_2) was 0.631kg/kg_{CSG}, forR-40 ($CClH_3$) was 0.378kg/kg_{CSG}, for Nitrogen (N_2) was 0.375kg/kg_{CSG}, forR-114 ($CClF_2$-$CClF_2$) was 0.625kg/kg_{CSG}, forR-114a (CCl_2-CF_3) was 0.581kg/kg_{CSG}, forR-115 ($CClF_2$-CF_3) was 0.477kg/kg_{CSG}, forR-124 ($CClFH$-CF_3) was 0.505kg/kg_{CSG}, forR-125 (CHF_2-CF_3) was 0.496kg/kg_{CSG}, forR-134 (CHF_2-CHF_2) was 0.505kg/kg_{CSG} and forR-134a (CH_2F-CF_3) was 0.478kg/kg_{CSG}. From the work of [38] it should be noted that, all adsorbents tested in this study have high GWP, also R-(11, 12, 13, 21, 22, 114, 115, 124) have high ODP.

The main output of this study is presented in Tables I and II. Throughout the literature on adsorption refrigeration working pairs, the state-of-the-art in the application there are many studies has been done theoretically and experimentally and the main findings are summarized as follows: The refrigerants R134a and R507a used by [7] have high global warming potential (GWP), also n-butane, hydrogen, methanol, ethanol and diethyl ether are highly flammable gases and ammonia is a highly toxic refrigerant. Also, from the work of [8] it can be noted that methanol is a combustible and toxic gas and ammonia is highly toxic gas. While for the work of [10] it can be counted that SO_2 and NO are very corrosive and toxic gases. Also, from the work of [11] it can be noted that the adsorbent PTP–OMC – I and II have a very low adsorption capacity and from the work of [12] it can be noted that CO_2 has a bad effect on central nervous system in the case of high concentration leakage from adsorption refrigeration systems. But it should be considered from the work of [13] that water adsorbate based refrigeration systems need very low operating pressure to prevent icing. While, it should be noted from the work of [14] that fluorobenzene is flammable and toxic gas. From the work of [17] it is remarked that all adsorbents used in it have high GWP and ozone depletion potential (ODP). From the data of [18] it is noted that, activated carbon has a very low adsorption capacity to water. Also the tested composite adsorbents have lower adsorption capacity than single adsorbent $CaCl_2$. From the data of [19] it is cleared that, the tested and studied pairs are not sufficient to be used in adsorption refrigeration systems, due to their low adsorption capacity. On the other hand depending on the work of [21], it is remarked that, R134a has a bad environmental effect due to its high GWP. From the work of [22] it is remarked that, methanol is a flammable gas and has an effect on global warming. From the work of [24] it should be considered that NH_3 is a very toxic gas. From the work of [26] it can be noted that, diethyl ether is highly flammable gas. It should be noted from the work of [31] that, ethanol is flammable and has bad effects on nervous system in case of high concentration leakage. From the work of [32] it can be counted that n-butane is a highly combustible gas. From the work of [36] it should be considered that, to prevent water icing, the adsorption system needed to operate with very low vacuum. From the work of [37] it can be remarked that, R-141b has very bed effect on environment, due to its high GWP and high ODP. From the work of [38] it should be noted that, all adsorbents tested in this study have high GWP, also R-(11, 12, 13, 21, 22, 114, 115, 124) have high ODP. Also from this state of art it is noted that all the adsorption capacity experimental tests were done on packed beds, without providing the design for efficient heat and mass transfer process between the adsorbent and the refrigerant. In real adsorption system efficient heat and mass transfer process leads to compact and less weight chiller design. The adsorption/desorption process net efficient heating and cooling for the adsorbent materials. The packed bed design does not provide efficient heating and cooling for the adsorbent materials. Therefore it should be designs that provide efficient heating and cooling for the adsorbent materials through distributing the adsorbent material over heat exchanger surface, to allow good heat and mass transfer between the adsorbent and the refrigerant.

III. CONCLUSION

This study presented and summarized the state-of-the-art of adsorption refrigeration working pairs and clarified the maximum adsorption quantity of different working pairs. It is found that the maximum adsorption capacity for the classical working pairs was 0.259 kg/kg for activated carbon/methanol and that for the modern working pairs was 2kg/kg for maxsorb III/R-134a.

Clearly, from the review of the published work the performance of the adsorption working pairs of adsorption cooling systems are still not satisfied and more research have to be done to develop an adsorption pair having a super sorption ability and less or no impact on the environmental. The main target of such good characteristics adsorption refrigeration working pairs are compact, efficient and reliable for long life performance adsorption refrigeration system. Also it can be concluded that, activated carbon powder adsorbent did not studied deeply and need more interest and use. Also, future researches need to be focused on designing the adsorption system that provide efficient heating and cooling for the adsorbent materials through distributing the adsorbent material over heat exchanger surface, to allow good heat and mass transfer between the adsorbent and the refrigerant.

TABLE I
SUMMERY AND COMPARISON BETWEEN ADSORPTION CHARACTERISTICS OF THE CLASSICAL ADSORPTION PAIRS

Adsorbent	Adsorbate	Maximum Adsorption Capacity (kg/kg)	Tads °C	P (bar)	ODP [39]	GWP [39]
activated carbon	Methanol	0.259 [6]	30	0.0523	0	2.8
silica gel	H_2O	0.116 [6]	30	0.09587	0	N A
zeolite13x	H_2O	0.236 [6]	30	0.09587	0	N A

TABLE II
SUMMERY AND COMPARISON BETWEEN ADSORPTION CHARACTERISTICS OF THE COLLECTED MODERN ADSORPTION PAIRS

Adsorbent	Adsorbate	Maximum Adsorption Capacity (kg/kg)	T_{ads} °C	P bar	ODP [39]	GWP [39]
activated carbon	H_2	0.055 [7]	30	6	0	5.8
activated carbon fibers	N_2	0.75 [7]	- 4	N A	0	N A
Maxsorb III	R134a	2 [7]	30	8	0	1300
Maxsorb III	R507	1.3 [7]	20	N A	0	3300
Maxsorb III	n-butane	0.8 [7]	35	2.3	0	4
activated carbon	CO_2	0.084 [7]	30	1	0	1
FAM-Z02	H_2O	0.2 [8]	30	N A	0	N A
porous coordination polymer	Methanol	0.19 [8]	30	N A	0	2.8
porous coordination polymer	H_2O	0.21 [8]	30	N A	0	N A
silica-LiCl	Methanol	0.6 [8]	30	N A	0	2.8
vermiculite-$BaCl_2$	NH_3	0.25 [8]	30	N A	0	0
activated carbon	NH_3	0.29 [9]	N A	N A	0	0
activated carbon	Ethanol	1.2 [9]	N A	N A	0	N A
Metal hydrides	H_2	0.073 [9]	N A	0.6	0	N A
expanded graphite- calcium chloride	NH_3	0.239 [9]	N A	N A	0	0
Zeolite-foam aluminum	H_2O	0.22 [9]	N A	N A	0	N A
Zeolite	N_2	0.04 [9]	0	1	0	N A
activated carbon	N_2	0.00756 [9]	30	1	0	N A
activated carbon fiber	SO_2	9.086 mmol/g [10]	50	0.52	0	N A
activated carbon fiber	NO	5.546 mmol/g [10]	50	0. 56	0	N A
activated carbon fiber	CO_2	4.629 mmol/g [10]	50	0. 65	0	1
polythiophene – carbon I	CO_2	0.12 [11]	25	1	0	1
polythiophene – carbon II	CO_2	0.125 [11]	25	1	0	1
attapulgite –LiCl	H_2O	0.44 [13]	30	$1.5*10^{-3}$	0	N A
Attapulgite	H_2O	0.2 [13]	N A	N A	0	N A
granular activated carbon	fluorobenzene (FB)	0.388 [14]	25	N A	N A	N A
NA	H_2O	0.7 [16]	27	N A	0	N A
NB	Ethanol	0.68 [16]	27	N A	0	N A
activated carbon	R-113	0.85 [17]	N A	0.5333	0.8	5000
activated carbon	R-141b	0.66 [17]	N A	0.9333	0.11	630
activated carbon	5FP	0.88 [17]	N A	0.0666	N A	N A
activated carbon	R-225cb	0.86 [17]	N A	0.4	0.033	620
activated carbon-silica gel-$CaCl_2$	H_2O	0.23 [18]	27	$9*10^{-3}$	0	N A
activated carbon	H_2O	0.02 [18]	27	$9*10^{-3}$	0	N A
zeolite 13X-$CaCl_2$	H_2O	0.404 [18]	25	$8.7*10^{-3}$	0	N A
$CaCl_2$	H_2O	0.9 [18]	N A	N A	0	N A
TiO2 (TNTs)	CO_2	0.269 mmol/g [19]	25	1	0	1
MOF-5	CO_2	0.092.4 [19]	23	N A	0	1
Zeolite13x	CO_2	1.77 mmol/g [19]	N A	N A	0	1
ZIF09	CO_2	0.2098 [19]	0	N A	0	1
Granular A C	R134a	1.68 [21]	25	N A	0	1300
(SBA-15)- $CaCl_2$	H_2O	0.7 [23]	50	N A	0	N A
NH_4Cl-$MnCl_2$	NH_3	0.747 [24]	30	N A	0	0
NaBr-$MnCl_2$	NH_3	0.649 [24]	30	N A	0	0
SWCNT	H_2	0.065 [25]	25	19.2	0	N A
SWCNT	CH_4	0.021 [25]	25	21	0	N A
SWCNT	N_2	0.019 [25]	25	19.2	0	N A
SWCNT	CO	0.042 [25]	25	20	0	N A
SWCNT	CO_2	0.1042 [25]	25	19.8	0	1
activated carbon	Diethyl - ether	$2.0028*10^{-3}$ [26]	35	0.309	0	N A
silica gel - $CaCl_2$(SWS-1L)	H_2O	0.275 [29]	30	N A	0	N A
$MgCl_2$	NH_3	0.38 [30]	35	2	0	0
$CaCl_2$	NH_3	0.97 [30]	35	4	0	0
$SrCl_2$	NH_3	0.87 [30]	35	2.5	0	0
$BaCl_2$	NH_3	0.18 [30]	35	1.5	0	0
Maxsorb III	Ethanol	1.2 [31]	20	N A	0	N A
Maxsorb III	n-butane	0.8 [32]	25	2.3234	0	4

Vermic-ulite - $BaCl_2$	NH_3	0.4 [33]	37	N A	0	0
activated carbon-$CaCl_2$	NH_3	0.78 [34]	30	N A	0	0
monolithic Carbon	NH_3	0.3837 [35]	25	N A	0	0
(MCM-41)- $CaCl_2$	H_2O	0.75 [36]	40	N A	0	N A
activated carbon fiber (ACF)	R-141b	0.69 [37]	25	N A	0.11	630
extruded activated carbon (EAC)	R-141b	0.62 [37]	25	N A	0.11	630
granular activated carbon (GAC)	R-141b	0.56 [37]	25	N A	0.11	630
activated alumina	R-141b	0.4 [37]	25	N A	0.11	630
Carbon molecular sieve	R-141b	0.385 [37]	25	N A	0.11	630
Nano-porous carbon (CSG)	R-11	0.735 [38]	22	0.9333	1.0	4,000
Nano-porous carbon (CSG)	R-12	0.644 [38]	22	0.9333	1.0	8,500
Nano-porous carbon (CSG)	R-13	0.492 [38]	22	0.9333	1.0	11,700
Nano-porous carbon (CSG)	R-21	0. 669 [38]	22	0.9333	0.04	210
Nano-porous carbon (CSG)	R-22	0.57 [38]	22	0.9333	0.055	1,700
Nano-porous carbon (CSG)	R-23	0.409 [38]	22	0.9333	N A	N A
Nano-porous carbon (CSG)	R-30	0.631 [38]	22	0.9333	N A	N A
Nano-porous carbon (CSG)	R-40	0.378 [38]	22	0.9333	N A	N A
nanoporous carbon (CSG)	N_2	0.375 [38]	22	0.9333	N A	N A
nanoporous carbon (CSG)	R-114	0.625 [38]	22	0.9333	1.0	9,300
nanoporous carbon (CSG)	R-114a	0.581 [38]	22	0.9333	N A	N A
nanoporous carbon (CSG)	R-115	0.477 [38]	22	0.9333	0.6	9,300
nanoporous carbon (CSG)	R-124	0.505 [38]	22	0.9333	0.022	480
nanoporous carbon (CSG)	R-125	0.496 [38]	22	0.9333	N A	N A
nanoporous carbon (CSG)	R-134	0.505 [38]	22	0.9333	N A	N A
nanoporous carbon (CSG)	R-134a	0.478 [38]	22	0.9333	0	1300

ACKNOWLEDGMENT

The first author would like to acknowledge Ministry of Higher Education (MoHE) of Egypt for providing a scholarship to conduct this study as well as the Egypt Japan University of Science and Technology (E-JUST) for offering the facility and tools needed to conduct this work.

REFERENCES

[1] L. Yong and R. Z. Wang. “Adsorption Refrigeration: A Survey of Novel Technologies”, Recent Patents on Engineering, Vol. 1, No. 1, 2007.

[2] I. Pilatowsky, R. J. Romero, C. A. Isaza, S. A. Gamboa, P. J. Sebastian and W. Rivera “Cogeneration Fuel Cell-Sorption Air Conditioning Systems”. Green Energy and Technology, Springer Publication 2011. First Edition.

[3] A. O. Dieng and R. Z. Wang “Literature review on solar adsorption technologies for ice-making and air conditioning purposes and recent developments in solar technology”. Renewable and Sustainable Energy Reviews vol. 5, ppt. 313–342, 2001.

[4] K. Habib, B. B.Saha, A. Chakraborty, S. Koyama and K. Srinivasan “Performance evaluation of combined adsorption refrigeration cycles”. International journal of refrigeration vol. 34,ppt. 129-137, 2011.

[5] State of the art – Survey on new solar cooling developments. IEA SHC Task 38 Solar Air Conditioning and Refrigeration. Subtask C1 Report, 31 October 2010.

[6] J. Y. San and W. M. Lin “Comparison among three adsorption pairs for using as the working substances in a multi-bed adsorption heat pump”. Applied Thermal Engineering 28,ppt. 988–997, 2008.

[7] A. A. Askalany, M. Salem, I. M. Ismail, A H H. Ali and M. G. Morsy “A review on adsorption cooling systems with adsorbent carbon”. Renewable and Sustainable Energy Reviews vol. 16,ppt. 493– 500, 2012.

[8] Y. I. Aristov, “Challenging offers of material science for adsorption heat transformation: A review”, Applied Thermal Engineering vol.50,ppt. 1610-1618, 2011.

[9] A. A. Askalany, M. Salem, I.M. Ismael, A.H.H. Ali, M.G. Morsy and B. B. Saha. “An overview on adsorption pairs for cooling”. Renewable and Sustainable Energy Reviews vol. 19, ppt. 565–572, 2013.

[10] X. Zhou, H. Yi, X. Tang, H. Deng and H. Liu. “Thermodynamics for the adsorption of SO2, NO and CO2 from flue gas on activated carbon fiber”. Chemical Engineering Journal vol. 200–202, ppt. 399–4042012.

[11] M. Bhagiyalakshmi, P.Hemalatha, M. Palanichamyand H. T. Jang “Adsorption, regeneration and interaction of CO2 with a polythiophene–carbon mesocomposite”. Colloids and Surfaces A: Physicochem. Eng. Aspects vol.374, ppt. 48–53, 2011.

[12] S. Jribi, A. Chakraborty, I. I. El-Sharkawy, B. B. Saha and S. Koyama “Thermodynamic Analysis of Activated Carbon- CO2 based Adsorption Cooling Cycles”. World Academy of Science, Engineering and Technology (2008) 43.

[13] C. Hai-jun, C. Qun, T. Ying, C. Xiu-jun and Y. Hu-qing “Attapulgite based LiCl composite adsorbents for cooling and air conditioning applications”. Applied Thermal Engineering vol.28, ppt. 2187–2193, 2008.

[14] M. F. Carvalho, A. F. Duque, I. C. Gonc and P.M.L. Castro “Adsorption of fluorobenzene onto granular activated carbon: Isotherm and bioavailability studies”. Bioresource Technology vol. 98, ppt. 3424–3430, 2007.

[15] I. Solmus, D. A. S. Rees, C.Yamalı, D. Baker and B. Kaftanoglu “Numerical investigation of coupled heat and mass transfer inside the adsorbent bed of an adsorption cooling unit”. International Journal of Refrigeration vol. 35, ppt. 652-662, 2012.

[16] Q. Cui, G. Tao, H. Chen, X. Guo and H. Yao “Environmentally benign working pairs for adsorption refrigeration”. Energy vol.30,ppt. 261–271, 2005.

[17] S. Tanada, N. Kawasaki, T. Nakamura and I. Abe “Adsorption Properties of CFC and CFC Replacements on Activated Carbon Containing Introduced Ionic Fluoride and Chloride”. Journal of Collide and Interface Science vol. 183,ppt. 143–147, 1996.

[18] Tso C.Y. and Chao C. Y.H. Activated carbon, silica-gel and calcium chloride composite adsorbents for energy efficient solar adsorption cooling and dehumidification systems. International Journal of Refrigeration 35 (2012) 1626 – 1638.

[19] X. Lia., H. Liu, D. Luo, J. Li, Y. Huang, H. Li, Y. Fang, Y. Xu and L. Zhu “Adsorption of CO2 on heterostructure CdS (Bi2S3)/TiO2 nanotube photocatalysts and their photocatalytic activities in the reduction of CO2 to methanol under visible light irradiation”. Chemical Engineering Journal vol. 180, ppt. 151 – 158, 2012.

[20] Z. Zhang, S. Xian, H. Xi, H. Wang and Z. Li “Improvement of CO2 adsorption on ZIF-8 crystals modified by enhancing basicity of surface”. Chemical Engineering Science vol. 66, ppt. 4878 – 4888, 2011.

[21] A. A. Askalany. M. Salem, I. M. Ismail, A. H. H. Ali and M. G. Morsy. “Experimental study on adsorption-desorption characteristics of granular activated carbon/R134a pair”. International Journal of Refrigeration vol. 35, ppt. 706-7132012.

[22] V. Baiju and C. Muraleedharan “Performance Study Of A Two Stage Solar Adsorption Refrigeration System”. International Journal of Engineering Science and Technology vol.3,ppt. 5754–5764, 2011.

[23] I. Glaznev, I. Ponomarenko, S. Kirik and Y. Aristov. “Composites CaCl2/SBA-15 for adsorptive transformation of low temperature heat: Pore size effect”. International Journal of Refrigeration vol. 34,ppt. 1244 – 1250, 2011.

[24] H. S. Bao, R. G. Oliveira, R. Z. Wang, L.W. Wang and Z.W. Ma "Working pairs for resorption refrigerator". Applied Thermal Engineering vol. 31, ppt. 3015 – 3021, 2011.

[25] G. P. Lithoxoos, A. Labropoulos, L. D. Peristeras, N. Kanellopoulos, J. Samios and I. G. Economou. "Adsorption of N2, CH4, CO and CO2 gases in single walled carbon nanotubes: A combined experimental and Monte Carlo molecular simulation study". The Journal of Supercritical Fluids vol. 55, ppt. 510 – 523, 2010.

[26] M. A. Al-Ghouti, I. Yousef, R Ahmad., A. M. Ghrair and A. A. Al-Maaitah "Characterization of diethyl ether adsorption on activated carbon using a novel adsorption refrigerator". Chemical Engineering Journal vol. 162, ppt. 234 – 241, 2010.

[27] Y. L. Liu, R.Z. Wang and Z.Z. Xia "Experimental study on a continuous adsorption water chiller with novel design". International Journal of Refrigeration vol. 28, ppt. 218–230, 2005.

[28] Z. Z. Xia, R. Z. Wang, D. C. Wang, Y. L. Liu, J.Y. Wu and C.J. Chen "Development and comparison of two-bed silica gel–water adsorption chillers driven by low-grade heat source". International Journal of Thermal Sciences vol. 48, ppt. 1017–1025, 2009.

[29] J.Y. San and H.C. Hsu "Performance of a multi-bed adsorption heat pump using SWS-1L composite adsorbent and water as the working pair". Applied Thermal Engineering vol. 29, ppt. 1606–16139, 2009.

[30] L. Wang, L. Chen, H. L. Wang and D. L. Liao "The adsorption refrigeration characteristics of alkaline-earth metal chlorides and its composite adsorbents". Renewable Energy vol. 34, ppt. 1016–1023, 2009.

[31] I. I. El-Sharkawy, B. B. Saha, S. Koyama, J. He, K. CNg. and C. Yap "Experimental investigation on activated carbon–ethanol pair for solar powered adsorption cooling applications". International Journal of Refrigeration vol. 31,ppt. 1407 – 1413, 2008.

[32] B. B. Saha, A. Chakraborty, S. Koyama, S. H. Yoon, I. Mochida, M. Kumja, C. Yap and K. C. Ng "Isotherms and thermodynamics for the adsorption of n-butane on pitch based activated carbon". International Journal of Heat and Mass Transfer vol. 51,ppt. 1582–1589, 2008.

[33] Y. Zhong, R. E. Critoph, R. N. Thorpe, Z. T. Telto and Y.I. Aristov "Isothermal sorption characteristics of the BaCl2–NH3 pair in a vermiculite host matrix". Applied Thermal Engineering vol. 27, ppt. 2455–2462, 2007.

[34] L. W. Wang, R. Z. Wang, Z. S. Lu, C.J. Chen and J.Y. Wu "Comparison of the adsorption performance of compound adsorbent in a refrigeration cycle with and without mass recovery". Chemical Engineering Science vol. 61, ppt. 3761 – 3770, 2006.

[35] Z. T. Telto and R. E. Critoph "Advanced solid sorption air conditioning modules using monolithic carbon–ammonia pair". Applied Thermal Engineering vol. 23, ppt. 659–674, 2003.

[36] M. Tokarev, L. Gordeeva, V. Romannikov, I. Glaznev and Y Aristov. "New composite sorbent CaCl2 in mesopores for sorption cooling/heating". Int. J. Therm. Sci. vol. 41, ppt. 470–474, 2002.

[37] S. H. Lin and Y. W. Chen "Gas-phase adsorption isotherms and mass transfer characteristics of 1,1-dichloro- 1-fluoroethane (HCFC- 141 b) by various adsorbents". Journal of Hazardous Materials vol. 57, ppt. 193-207, 1998.

[38] R. K. Mariwala, M. Acharya and H. C. A Foley "Adsorption of halocarbons on a carbon molecular sieve". Microporous and Mesoporous Materials vol. 22, ppt. 281-288, 1998.

[39] I. Dincer and M. Kano˘glu "Refrigeration Systems and Applications". A John Wiley and Sons, Ltd., Publication.2010, Second Edition.