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# Adsorption Refrigeration Technologies

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## Abstract

This chapter introduces a comprehensive overview about the principles, challenges and applications of adsorption refrigeration systems (ARSs), as a promising sustainable solution for many of cooling and heating applications. In addition to the features and the basics of ARSs, the following topics have been covered such as characteristics of working pairs, trends in improving the heat and mass transfer of the adsorber; advanced adsorption cycles and performance and operational data of some adsorption refrigeration applications. In some details, the operating range and the performance of ARSs are greatly affected by the employed working adsorbent/refrigerant pairs. Therefore, the study, development and optimum selection of adsorbent/refrigerant pairs, particularly the composite adsorbents, can lead to improving the performance and reliability of ARSs. Regarding the enhancement of heat and mass transfer in the adsorbent bed, two methods are commonly used: one is the development of adsorbents through different coating technologies or new materials such as metal-organic frameworks, and the second is the optimization of the adsorber geometrical parameters and cycle modes. Finally, a brief on some adsorption chillers applications have started to find their share in markets and driven by solar or waste heats.

**Keywords:** adsorption refrigeration, solar air conditioning, heat recovery, metal-organic frameworks, adsorbent bed

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## 1. Introduction

Utilization of thermally driven refrigeration systems can reduce both direct and indirect emissions of the greenhouse gases and can contribute to a sustainable solution that meets

the escalating demand of the cooling equipment. The electrically driven refrigeration systems have high coefficients of performance (COP), low weights and small sizes compared to their current alternatives. However, they rely on a high-grade energy produced mostly from burning fossil fuels in thermal power plants and employ environmentally harmful refrigerants. Meanwhile, the increased demand of the electricity consumed by these refrigeration systems during the hot summer days leads to a considerable increase in the peak loads on the electricity grids causing increasing costs, blackouts and brownouts, and represents a great challenge in many of the developing countries. Thermally driven refrigeration technologies appear to be a promising alternative solution to limited energy resources and ecological problems. Such systems can utilize directly low-grade thermal energies or waste heat recovered from industrial processes, and use environmentally safe refrigerants as systems presented in [1]. The most interesting technologies are called 'sorption cooling systems' including desiccant, absorption and adsorption refrigeration systems (ARSs). Although the most cited drawbacks for sorption refrigeration systems are the high initial cost, heavy weight, large size, and the possible need for backup cooling systems, the benefits are nonetheless obvious [2]. They can employ natural substances as working fluids (water, ammonia, etc.), and use the available heat sources and clean energy more efficiently to produce refrigeration effect. For examples, burning fuels can be used directly to drive the sorption refrigeration systems; thereby the inefficiencies associated with the conversion of thermal energy to electricity and its transmission to the consumers can be eliminated. Solar refrigeration systems which offer the features of minimal operating cost, environmental preference, transforming solar energy directly into cooling power and maximum solar radiation are generally in phase with the peak demand of the cooling loads. Recovering the waste heats in industrial applications could improve the overall performance of such systems. Adsorption refrigeration systems (ARSs), one of these heat-driven systems, have a distinct advantage in their ability to be driven by relatively lower temperature heat sources as well as not involving any moving parts in the refrigerant cycle which means minimal maintenance and more durability. Nevertheless, there are two main drawbacks that limit their commercialization: the intermittently working principle (discontinuous cooling effect) and the low cycle COP. The latter is influenced by poor mass and heat transfer of the adsorbent bed, the heart of the cycle, which plays the role of compressor in conventional refrigeration cycles [3]. Historically, the earliest record of the adsorption phenomena for refrigeration purpose was introduced in 1848 by Faraday who found that the cooling capacity could be generated when silver chloride adsorbed ammonia. Compression refrigeration systems were developed starting from 1930s after Freon was developed. In the 1970s, the energy crisis took hold, and in the last four decades, the environmental impacts of conventional refrigeration systems had been recognized worldwide, which offered a great chance for the development of such ARSs. The objective of this chapter is to introduce a comprehensive overview about the principles, application and challenges of ARSs. In addition to the description of the basic adsorption system, the chapter covers the following topics such as characteristics and development of working pairs; trends in improving the heat and mass transfer of the adsorber; advanced adsorption cycles; and state of the art adsorption cooling applications.

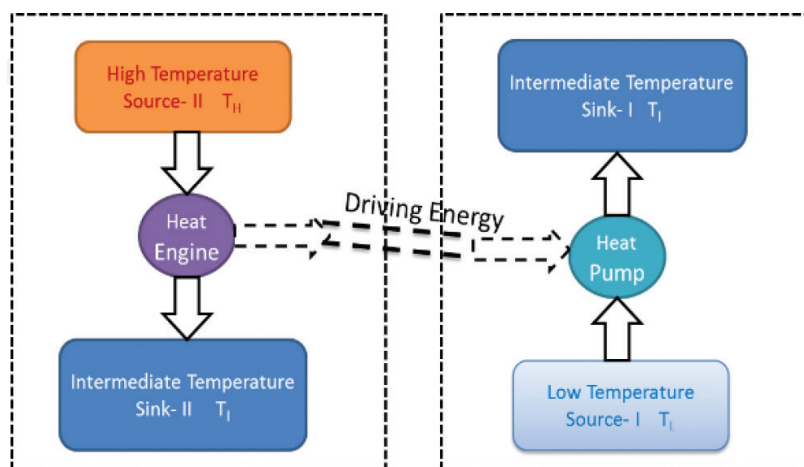
### 1.1. Basic adsorption refrigeration cycle

From the thermodynamics point of view, a basic adsorption refrigeration cycle can be considered as two separate cycles. One a heat engine and the other is a refrigerator (or heat pump), and operates with three temperature levels. It is assumed that the work produced by the heat engine is used to drive the refrigerator as illustrated in **Figure 1** [3].

$$\text{COP}_{ref} = \frac{Q_{eva}}{Q_{preheating} + Q_{des}} = \frac{1 - \left(\frac{T_L}{T_H}\right)}{\left(\frac{T_L}{T_I}\right) - 1} \quad (1)$$

The basic ARS consists of four main components: an adsorbent bed, which contains highly porous bodies called *adsorbent* with tremendously large internal surface (such as silica gel, activated carbon, zeolite, etc.) having strong adsorptive property to a specified gas or gases called *adsorbate/refrigerant* (such as water, ammonia, methanol, etc.). The adsorbent is normally packed on a metal surface which is required to conduct the heat transferred from/to a heat transfer fluid (HTF) (usually by heating and cooling water) that flows in the bed. The other 3 cycle components are: a condenser, an evaporator and an expansion valve. They are similar to those normally used in a simple conventional refrigeration cycle and play the same roles with an electrically driven compressor, so that the adsorbent bed is called a thermally driven compressor which circulates the refrigerant in an adsorption cycle by periodic switching between heating and cooling HTFs. The Carnot COP of a basic ARS can be expressed as Eq. (1) [4]:

A simple adsorption refrigerator produces cooling effect by subjecting the adsorbent bed to four sequential processes which are pre-heating, desorption, pre-cooling and adsorption as shown in **Figure 2**. Clapeyron diagram ( $\ln P$  vs.  $-1/T$ ) with respect to isosteres of adsorbent-adsorbate pair in **Figure 3** is typically used to illustrate the four ideal thermodynamic processes of an adsorbent bed and calculate the cycle COP theoretically. In this ideal cycle, the



**Figure 1.** Representation of the thermodynamics cycle of ideal ARS.

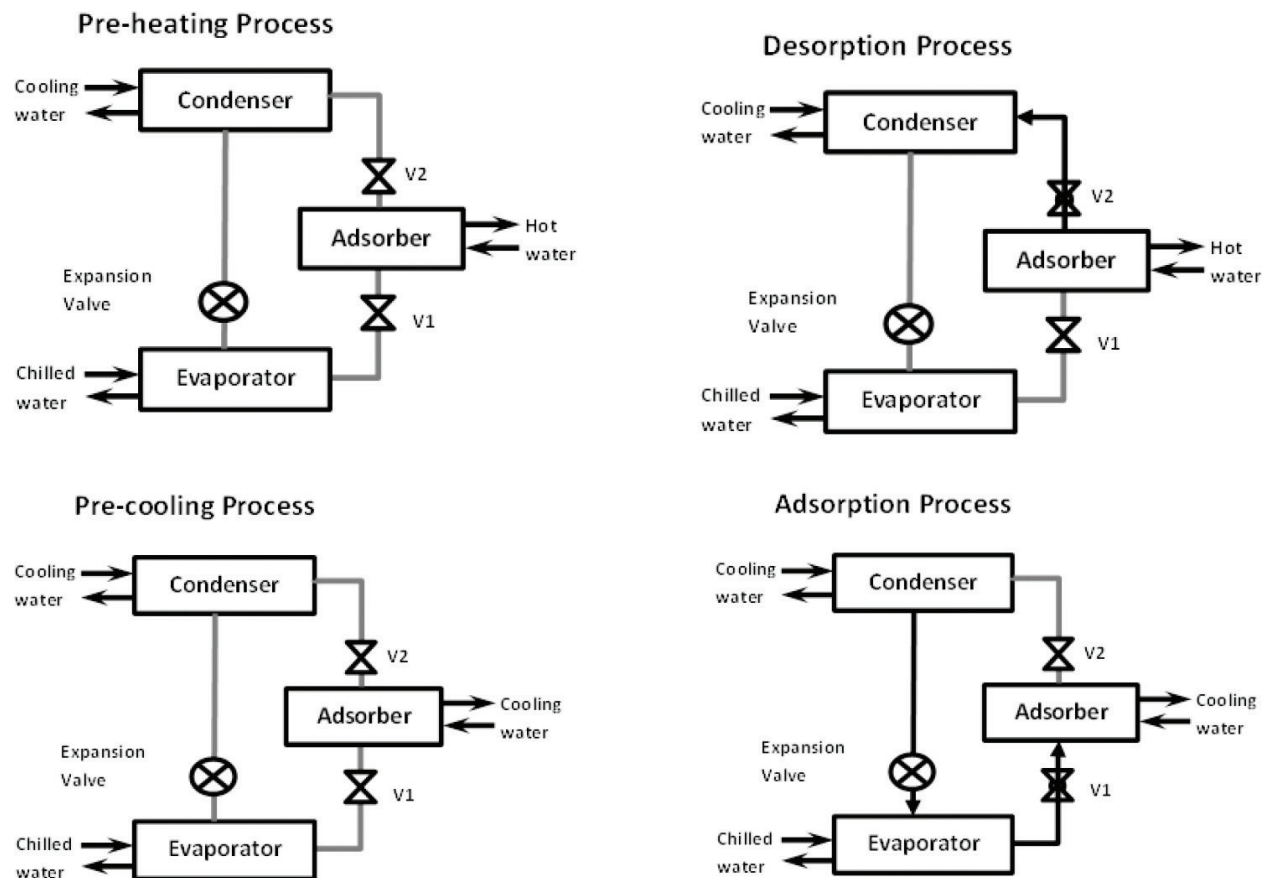


Figure 2. The flow diagrams of the basic adsorption cooling system under one complete cycle.

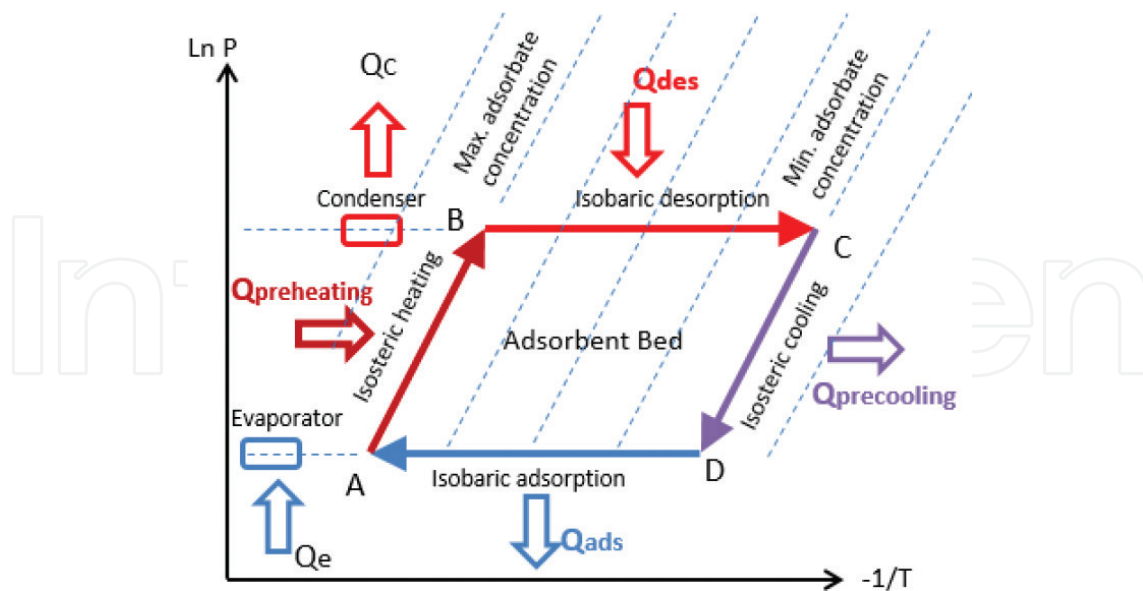


Figure 3. Clapeyron diagram of an ideal adsorption refrigeration cycle.

adsorber (adsorbent bed) operates between the two constant pressures, the condenser and evaporator pressures, and the two (minimum and maximum) adsorbate concentration levels. These four ideal processes can be described as follows:

**Pre-heating process (A–B):** In this heating and pressurization period, the valves between the adsorbent bed and both of the condenser and the evaporator (V1 and V2) are closed, and the adsorbent bed is operated as a closed system that is subjected to heat source at temperature of  $T_H$  by means of heating HTF. Meanwhile, the bed temperature increased sensibly which induces the vapor pressure inside the bed also to be increased. Whereas, the total amount of refrigerant in adsorbed phase remains constant at the maximum concentration. This process lasts until the vapor pressure reaches the condenser pressure at point B.

**Desorption process (B–C):** After the first process, the heating of the adsorbent bed is continued while the valve (V2) connecting the bed with the condenser is opened. The bed temperature is gradually increased, which induces a part of refrigerant which is in adsorbed phase to leave the solid surface of adsorbent to be in a vapor phase in a process called ‘desorption process’. Then this desorbed vapor flows into the condenser and condenses there. The vapor pressure in the bed is considered equal to the condenser pressure during this period which is ended when the adsorbed amount reaches the minimum concentration level.

**Pre-cooling process (C–D):** After the bed reaches the maximum temperature in the cycle at point C, the cooling and depressurization period for the bed is started, and the two valves (V1 and V2) are set closed. The temperature is then decreased which induces the pressure inside the adsorber to be reduced to the evaporator pressure level by the end of this process.

**Adsorption process (D–A):** In the last period in which only the effective cooling occurs, the valve between the adsorber and the evaporator is opened, and the adsorber is continuously subjected to cooling by means of cooling HTF which induces an adsorptive vapor to accumulate on the adsorbent surface and converted to a new phase called ‘adsorbed phase’ in a process named ‘adsorption process’. Then, the vaporized vapor in the evaporator, which gives the cooling effect, is directed to the adsorber to take place in the adsorptive vapor. Cooling for the adsorbent bed is required in this process to release the associated heats from both the heating period and the adsorption process.

## 1.2. Performance indicators

The average cooling capacity  $Q_{eva}$ , heat added  $Q_{heat}$ , SCC and COP can be defined for an adsorption refrigeration chiller as follows:

$$Q_{eva} = \frac{1}{t_{cycle}} \int_0^{t_{cycle}} \dot{m}_{chw} c_{chw} (T_{chw,i} - T_{chw,o}) dt \quad (2)$$

$$Q_{heat} = \frac{1}{t_{cycle}} \int_0^{t_{cycle}} \dot{m}_{hw} c_{hw} (T_{hw,i} - T_{hw,o}) dt \quad (3)$$

$$SCC = \frac{Q_{eva}}{M_s} \quad (4)$$

$$COP = \frac{Q_{evap}}{Q_{heat}} \quad (5)$$

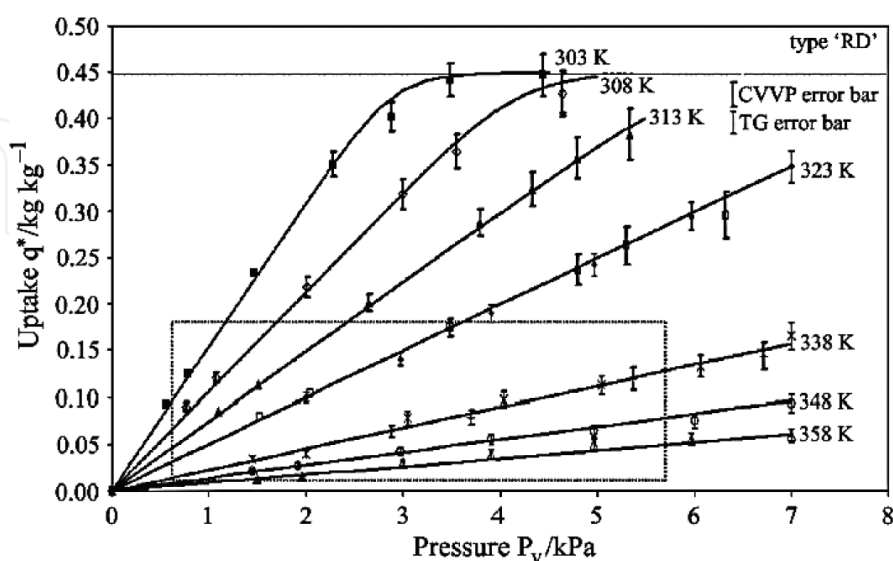
where  $M_s$  is the total amount of adsorbent packed in the adsorbers.



## 2. Working adsorbent/refrigerant pairs

The overall performance as well as the design and operating parameters for an ARS are greatly affected by the employed working adsorbent/refrigerant pairs. In general, good adsorbents should have wider range of adsorption capacity with temperature variation, higher heat and mass transfer properties, along with thermal stability and low susceptibility to contamination. In addition, distinctive properties of a refrigerant should be examined, and that include heat of vaporization, thermal conductivity, boiling point and working pressures, reactivity and stability, toxicity, environmental impact and freezing point. The adsorption capacity of an adsorbent-refrigerant pair is commonly determined from plots known as adsorption isotherms as shown in **Figure 4** [5]. These isotherms give the amount of adsorbed mass taken up by the adsorbent, after reaching the thermodynamic equilibrium, as a function of pressure at constant temperatures. Accordingly, adsorbent-adsorbate pairs and their developments can be compared based on their isotherms. However, when the adsorbent domain undergoes transient operating conditions, a kinetic model is required to define the mass transfer kinetics and gives the instantaneous amount of adsorbate through a relation with the equilibrium uptake that is given by the isotherms. Mass transfer kinetics is a catch-all term related to intra-particle mass transfer resistance. The increase in the adsorption capacity increases capability of an ARS to have a large cooling capacity, where it sets up the total amount of refrigerant that can be adsorbed in a cycle. However, faster mass transfer kinetics is required to insure higher cooling capacity as it controls the duration of the adsorption cycle.

The most commonly used adsorbent/refrigerant pairs are silica gel/water, zeolite/water, activated carbon/methanol, activated carbon/ammonia, calcium chloride/ammonia and composite adsorbent/ammonia. In general, according to the nature of the forces involved in the adsorption process, they are classified into three categories such as physical, chemical and composite adsorbent/adsorbate pair.



**Figure 4.** Isotherms for type RD silica gel-water pair [5].

## 2.1. Physical adsorbent-adsorbate pair

The physical adsorbents that are used in ARSs rely on van der Waal's forces to contain adsorbate. Three adsorbent-adsorbate pairs are generally considered to be the best available in applications:

### 2.1.1. Silica gel-water systems

Silica gel is an amorphous silicon dioxide,  $\text{SiO}_2$ , made synthetically from sodium silicate, and has a granular, vitreous and highly porous form. The high-density silica is the common type of silica gel used in adsorption systems such as Fuji Davison types 'A' and 'RD' silica gel, which have pore diameter in the range of 2.0–3.5 nm, the pore volume is 0.3–0.4  $\text{cm}^3/\text{g}$  and the specific surface area is 400–700  $\text{m}^2/\text{g}$  [6]. The other types of silica gel with relatively high pore sizes can be used as a host material in composite adsorbents. The thermodynamics characteristics of silica gel-water working pair were investigated experimentally by several researchers as in [5, 7], and the empirically determined parameters for the isotherm equations had been calculated from the experimental data. The performance of the two-bed silica gel-water was evaluated experimentally and analytically by several researchers [8–10].

In general, the main advantage of silica gel over other adsorbents is that the regeneration temperature is typically 85°C which makes such system to be suitable for solar energy use and low temperature waste heat sources. Moreover, it could be as low as 50°C when multi-stage configuration system is applied [11]. In such case, for non-regenerative cycle, the dynamic losses due to the heat capacities of the adsorber components will be reduced which lead to higher COPs since the adsorbent itself and the container vessel do not need to be heated to high temperatures. However, desorption temperature must not be too high. If it is higher than 120°C, silica gel will be destroyed. The adsorption heat is relatively higher than activated carbon pair between 2500–2800 kJ/kg. Also, silica gel porosity level is lower than activated carbon (100–1000  $\text{m}^2/\text{g}$ ). The maximum adsorption capacity at equilibrium could be between 0.35 and 0.4 kg/kg silica gel, while the net change in the instantaneous amount of adsorbate may not exceed 0.1 kg water/kg silica gel under typical operating conditions which is low. Another drawback is the limitation of evaporating temperature due to the freezing point of water and the uptake also is effected badly under a very low vacuum, that make silica gel-water refrigeration system be better to be applied in the air conditioning applications with large chilled water flow rates.

### 2.1.2. Zeolite-water systems

Zeolites are microporous, alumina silicate crystals composed of alkali or alkali soil. The zeolite-water working pair has a wide range of desorption temperature (70–250°C). Due to its stable performance at high temperatures, the adsorber can be directly heated by the exhaust gases from engines. Therefore, the zeolite-water system is simpler than that one driven by the hot water. However, the adsorption heat of zeolite-water is higher than that of silica gel-water, between about 3300 and 4200 kJ/kg [12], which will lead to low COPs, in addition to the drawbacks associated with using the water as a refrigerant. Several studies had been



presented experimentally and theoretically to investigate and improve the performance of zeolite-water adsorption system particularly for vehicle air conditioning.

### 2.1.3. Activated carbon (ammonia/methanol) systems

Activated carbon is a form of carbon that has a large specific area available for adsorption approximately between 800 and 1500 m<sup>2</sup>/g for most used carbon. Initially, raw materials such as coal, lignite, wood, nut shells and synthetic polymers undergo number of special pyrolysis or chemical treatment at high temperatures (700–800°C) to produce activated carbons. They can be produced in many forms including powders, microporous, granulated, molecular sieves and carbon fibers. Activated carbon has advantages of that: a relatively low adsorption heat among the other types of physical adsorbent pairs (1800–2000 kJ/kg), low adsorption heat is beneficial to the system's COP because the majority of heat consumption in the regeneration phase is the adsorption heat [12], higher surface reactivity, suitable pore size [13] and large surface area. However, the thermal conductivity of activated carbon is poor and is near to the insulation material. For example, ACF-methanol system with a higher specific adsorption reaches up to 0.55 kg/kg<sub>ads</sub> and good mass transfer characteristics where void fraction of ACF layer is more than 0.90%, but the measured thermal conductivity is as low as 0.0893 W/(mK) [14]. The carbon physical characteristics could be optimized to obtain the best performance of ARSs.

#### a. Activated carbon-ammonia

While most of adsorbent-adsorbate pairs operate under high vacuum, an activated carbon-ammonia pair system has a high working pressure (about 1600 kPa when the condensing temperature is 40°C). So, permeability of sorbent is not critical and it can be easier and more applicable than sub-atmospheric systems. It is also more suitable than the activated carbon/methanol pair for heat sources of 200°C or higher. The drawbacks of this working pair are the toxicity and pungent smell of ammonia.

#### b. Activated carbon-methanol

Large adsorption capacity of activated carbon-methanol pair has adsorption capacity of about 0.45 kg/kg<sub>ads</sub>. Low regeneration temperature can be used to drive ARS employing activated carbon-methanol pair (about 100°C). On the other hand, it should not be used with regeneration temperature higher than 120°C, where activated carbon will catalyze methanol to decompose into dimethyl ether at a temperature more than 150°C, and operating pressure of the system will be sub-atmospheric and that requires assistant vacuum system.

## 2.2. Chemical adsorbents-adsorbate pair

Chemical adsorbents sorb the refrigerants differently than physical adsorbents where the strong chemical bond between the adsorbent and the refrigerant takes place in chemical adsorption. The uptake in the chemical adsorbents is not limited by the surface area of the material, which generally leads to higher mass transfer kinetics when compared to physical adsorbents. The metal chlorides are commonly used as chemical adsorbents due to their high

adsorption capacity, and they involve calcium chloride ( $\text{CaCl}_2$ ), strontium chloride ( $\text{SrCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), barium chloride ( $\text{BaCl}_2$ ), manganese chloride ( $\text{MnCl}_2$ ) and cobalt chloride ( $\text{CoCl}_2$ ), among others. For example, in  $\text{CaCl}_2$ /ammonia pair, 1 mole calcium chloride can adsorb 8 moles ammonia [15].

Generally, chemical adsorbents have very large uptakes with specific adsorptions approaching  $1 \text{ kg/kg}_{\text{ads}}$  in some cases, and desorption temperatures varying from 40 to  $80^\circ\text{C}$  which are very promising. However, chemical adsorption systems stability is lower than that for physical adsorption systems due to agglomeration and swelling phenomena, which are common in chemical adsorbent beds. This instability reduces heat and mass transfer which limits the cooling capacities of chemical adsorbents. Consequently, heat-driven chillers utilizing these adsorbents have been less common than those using physical adsorbents. To overcome this problem, the porous heat transfer matrixes were put forward for the improvement of mass transfer as well as the heat transfer by using composite adsorbents.

### 2.3. Composite adsorbents-adsorbate pair

Composite adsorbents, also called “Salt in Porous Matrix (CSPM)” represent the promising solution of aforementioned drawbacks associated with pure physical and chemical adsorbents. Thus, many of these composites, which are typically made of porous media and chemical adsorbents, have been developed synthetically to be applied in adsorption refrigeration systems as in Refs. [16–18]. In such composites, porous media work on improving the heat and mass transfer properties of the chemical adsorbents along with limiting the swelling characteristics of the chemical adsorbents, while the chemical adsorbents increase the refrigerant uptake of the adsorbent pair. The common examples of these composites are combinations of metal chlorides and AC, ACF, expanded graphite, silica gel or zeolite. For example, silica gel and chlorides/water which are known as selective water sorbents (SWSs) which are tested and studied by Aristov et al. [6]. Composite adsorbents of silica gel and chloride are usually produced using the impregnation method. The silica gel is immersed in a chloride salt solution and is then dried to remove the water. There are also four types of porous media were used with chlorides to produce composite adsorbents/ammonia: activated carbon, activated carbon fiber, expanded graphite or vermiculite.

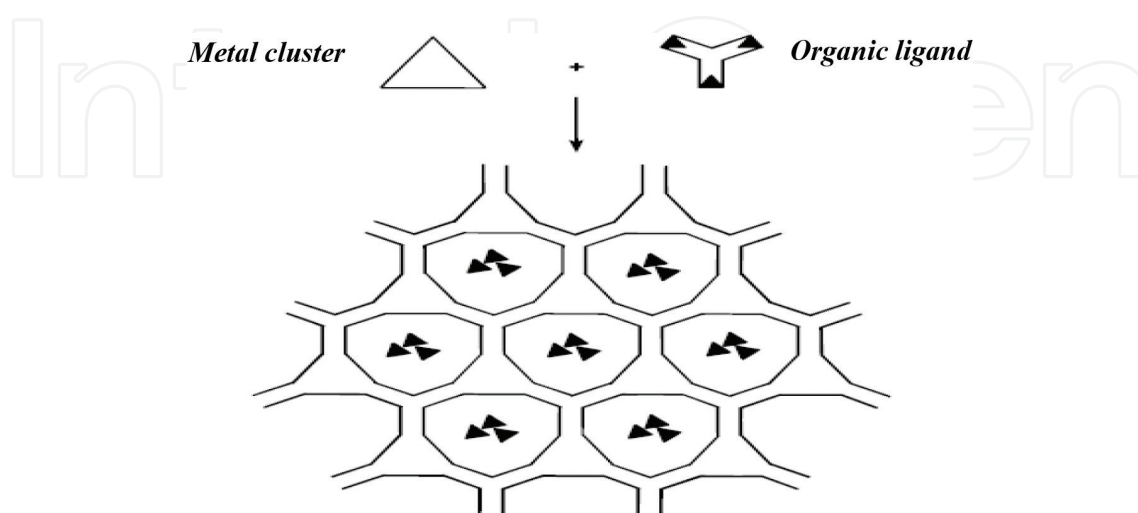
### 2.4. Novel adsorbent materials: metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are highly crystalline porous material that are widely regarded as promising materials for various applications such as catalysis [19], gas separation [20] and gas storage [21]. The high crystallinity of MOFs can be highlighted through the description of MOF-5 structure which was once described as “The zinc carboxylate cluster with the six carboxylate carbons forming a regular octahedron but with tetrahedral symmetry was elegantly beautiful especially when linked in such regular arrays like terracotta warriors” [22]. Usually, the approach of assembling new frameworks out of molecular building blocks or secondary building blocks held together by strong bonding has been considerably used in designing new materials even though it is a challenge to control the assembly of the basic building blocks in the solid state and thus predicting of the resulting structure. Based

on the same concept or what is called the reticular synthesis, MOFs are designed based on the assembly of organic units and metal clusters as secondary building units (SBUs) to build the robust complex structures (**Figure 5**) [23]. Compared to conventional microporous inorganic materials such as zeolites and silica gel, MOFs were found to be flexible regarding controlling their architecture and functionalization of the pores [24]. Such tunable properties have given the lead to MOFs over conventional adsorbents as they offer high stability and porosity as shown in **Figure 6**. As mentioned above, these exceptional properties made this class of materials very interesting in a number of applications. Adsorption heat pumping for cooling applications has attracted a massive research over the past few years. For decades, the adsorption cooling application was mainly based on silica gel, activated carbon and zeolites which suffer from the limited adsorption capacity. The next section will discuss the different MOF materials with different refrigerants for cooling applications.

#### 2.4.1. MOFs-water pair

Water is an environment friendly refrigerant with high latent heat of evaporation and high heat and mass transfer properties. Water-based adsorption systems use adsorbents like silica gel and zeolites which have limited water uptake capabilities (up to  $0.3 \text{ g}_w/\text{g}_{\text{ads}}$ ) leading to low specific cooling power. The introduction of metal-organic frameworks (MOFs) material for adsorption cooling application allowed an improvement in the performance of the systems due to the high-water uptake that can reach up to  $1 \text{ g}_w/\text{g}_{\text{ads}}$  and the potential of using low temperature waste heat or solar collectors as primary energy sources. Shi et al. [25] showed that using CPO-27(Ni) MOF material (a max water uptake of  $0.45 \text{ g}_w/\text{g}_{\text{ads}}$ ) for automotive air conditioning can outperform SAPO 34 zeolite material in terms of specific cooling power. They showed that CPO-27(Ni) produced specific cooling power of  $440 \text{ W kg}^{-1}$  at a desorption temperature of  $130^\circ\text{C}$  and a cycle time of 900 s compared to  $310 \text{ W kg}^{-1}$  for SAPO-34 at the same operating conditions. Numerous metal-organic framework materials have been studied to investigate their water adsorption capacity, **Figure 7** shows maximum water uptake of a number of MOFs that were investigated for adsorption cooling applications at  $25^\circ\text{C}$ .



**Figure 5.** Schematic representation of how the framework is formed [47].

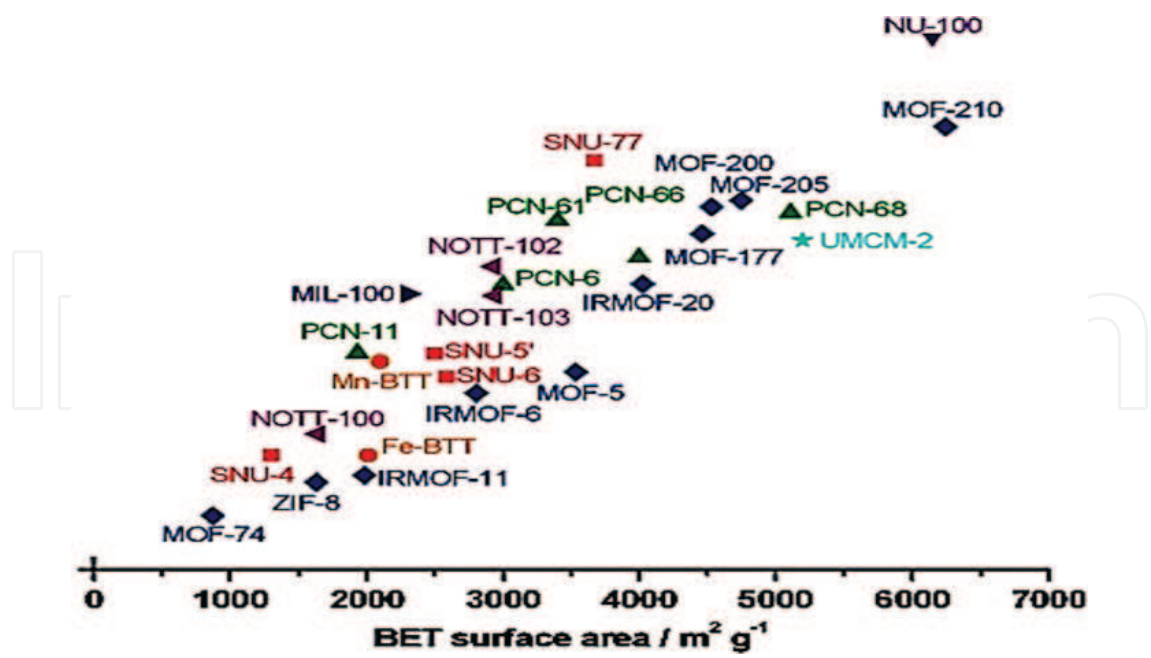


Figure 6. BET surface area comparison between some reported MOFs and zeolite [48, 49].

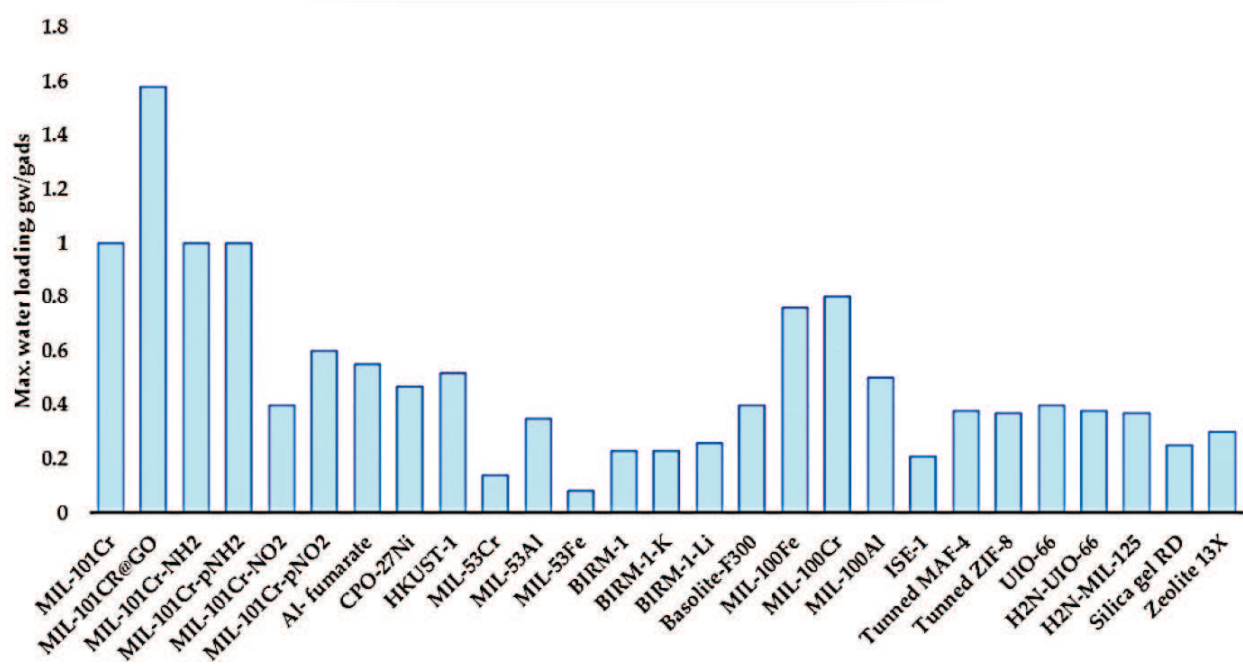


Figure 7. Maximum water uptake comparison between some reported MOFs, silica gel and zeolite.

Ehrenmann et al. [26] showed that MIL-101Cr can adsorb up to  $1 \text{ g}_w/\text{g}_{\text{ads}}$  with high performance stability, also the heat of adsorption value was near the evaporation enthalpy of water, meaning that the interaction energy with the framework was believed to be very low compared to other materials used so far, like zeolites and hence the material do not require high regeneration temperature. A further modification was investigated by Khutia et al. [27] as



the water loading capacity of four nitro or amino-functionalized MIL-101Cr materials (fully and partially functionalized) was assessed for heat transformation applications. The fully aminated MIL-101Cr-NH<sub>2</sub>, and partially aminated MIL-101Cr-pNH<sub>2</sub>, showed the best water loadings (about 1.0 g<sub>w</sub>/g<sub>ads</sub>) and proving the weak host-guest interactions and hence a lower regeneration temperature is required. Elsayed et al. [25] further improved the thermal conductivity and the water vapor capacity of MIL-101(Cr) to be used in adsorption heat pump application through using hydrophilic graphene oxide. Two methods have been used to develop MIL-101(Cr)/GrO composites. It was shown that introducing low amounts of GrO (2%) to the neat MIL-101(Cr) enhanced the water adsorption characteristics at high relative pressure but enhanced the heat transfer properties by 20–30% while using more than 2% of GrO reduced the water adsorption uptake but significantly enhanced the thermal conductivity by more than 2.5 times. Yan et al. [28] managed to improve the performance of the material through developing another composite (MIL-101@GO) of MIL-101(Cr) and graphite oxide (GO) with high-water vapor capacity for adsorption heat pumps (AHPs). It showed that MIL-101@GO possessed a super-high adsorption capacity for water vapor up to 1.58 g<sub>w</sub>/g<sub>ads</sub>. This superior water vapor adsorption/desorption performance make MIL-101@GO a promising candidate as the water vapor adsorbent for adsorption heat pumps (AHPs) process. Another factor that was studied was the effect molding on the water adsorption properties of MIL-101(Cr) after pressing the prepared powder into a desired shape which was investigated by Rui et al. [29]. It showed that the forming pressure has a large influence on pore structure of shaped MIL-101, as the forming pressure increases from 3 to 5 MPa, the equilibrium adsorption capacity of water is up to 0.95 g<sub>w</sub>/g<sub>ads</sub> at the forming pressure of 3 MPa. Other types of MOFs such as Al fumarate was investigated by Jeremias et al. [30] in the form of coating on a metal substrate via the thermal gradient approach. It was concluded that Al fumarate is a promising adsorbent for heat pumping applications as it can be regenerated at low temperature as low as 60°C with a water loading difference higher than 0.5 g<sub>w</sub>/g<sub>ads</sub>. Fadhel et al. [31–33], generated cooling effect from using aluminum fumarate and MIL-101(Cr) in different multi-bed water adsorption systems. The performance was compared to other adsorbent materials such as AQSOA-Z02 and conventional silica gel. The isostructural CPO-27(Ni) was compared to aluminum fumarate by Elsayed et al. [34]. It was highlighted that the CPO-27(Ni) outperformed the aluminum fumarate at low evaporation temperatures, while the aluminum fumarate was more suitable for applications requiring high evaporation temperature. It was also mentioned that CPO-27(Ni) is suitable for systems operated with high desorption temperature while on the contrary aluminum fumarate can be regenerated at low desorption temperatures.

The performance of a number of MOFs such as HKUST-1 and MIL-100(Fe) was investigated and compared to silica gel RD-2060 by Rezk et al. [35]. They showed that HKUST-1 performed better than silica gel RD-2060 with an increase of water uptake of 93.2%, which could lead to a considerable increase in refrigerant flow rate, cooling capacity and/or reducing the size of the adsorption system. However, MIL-100(Fe) MOF showed reduced water uptake comparable to silica gel RD-2060 for water chilling applications with evaporation at 5°C. These results highlight the potential of using MOF materials to improve the efficiency of water adsorption cooling systems. Other MOFs such as MIL-53(Cr), MIL-53(Fe), Birm-1,

Birm-1(K) and Birm-1(Li) showed water uptake of 0.14–0.35  $\text{g}_w/\text{g}_{\text{ads}}$  which is lower than the water adsorption capacity of HKUST-1, proving that HKUST-1 regarding to the water capacity outperform conventional porous materials such as silica gel and other MOF materials [36], comparing HKUST-1 with other zeolite materials like SAPO-34 and AIPO-18 showed that the best SAPO-34 samples had a water uptake of 0.253  $\text{g}_w/\text{g}_{\text{ads}}$  which is a factor of 4.9 larger compared to the reference silica gel. Those results were only exceeded by the best AIPO-18 sample with a measured water uptake of 0.254  $\text{g}_w/\text{g}_{\text{ads}}$  for the low driving temperatures. This equaled an improvement by a factor of 6.2. For driving temperature of 140°C, the highest water uptake was found for the metal-organic framework HKUST-1 [37]. Other MOFs such as MIL-100 (Fe and Al) with a water uptake of 0.76 and 0.5  $\text{g}_w/\text{g}_{\text{ads}}$  were found to be also very interesting candidates for thermally driven, sorption-based chilling or heat pump systems [38, 39]. A 3D MOF material (ISE-1) was found to have water loading of 0.210  $\text{g}_w/\text{g}_{\text{ads}}$  which was found to be larger than other five zeolites in that study and of the reference silica gel demonstrating the potential of MOF materials for use in adsorption heat pumping processes [40]. MIL-53(Al), MIL-100(Fe) and ZIF-8 were compared with the previous materials and were found to have a water uptake higher than 0.3  $\text{g}_w/\text{g}_{\text{ads}}$  proving that MOFs are a very promising class of materials for the use in adsorption heat pumping/cooling processes [41, 42]. The amino-functionalized MOFs UiO-66 and MIL-125 ( $\text{H}_2\text{N}$ -UiO-66 and  $\text{H}_2\text{N}$ -MIL-125) featured also very promising  $\text{H}_2\text{O}$  adsorption isotherms due to their enhanced hydrophilicity with a water load of  $\approx 0.4 \text{ g}_w/\text{g}_{\text{ads}}$  and were considered to be especially beneficial for the intended heat pump application [43].

#### 2.4.2. MOFs-ethanol pair

Saha et al. [44] presented experimental and theoretical investigations of adsorption characteristics of ethanol onto metal-organic framework namely MIL-101(Cr). The experiments have been conducted within relative pressures between 0.1 and 0.9 and adsorption temperatures ranging from 30 to 70°C, which are suitable for adsorption cooling applications. Adsorption isotherm data exhibit that 1 g of MIL-101(Cr) can adsorb as high as 1.1 g of ethanol at adsorption temperature of 30°C. The experimental results showed that the studied pair would be a promising candidate for developing high performance cooling device. Rezk et al. [45] experimentally investigated the ethanol adsorption characteristics of six MOF materials namely CPO-27(Ni), MIL-101(Cr), HKUST-1, MIL-100(Fe), MIL-53(Cr) and MIL-100(Cr) compared to that of silica gel as a conventional adsorbent material that is widely used in commercial adsorption systems. The results revealed that MIL-101(Cr) have shown superior performance with uptake value of 1.2  $\text{g}_w/\text{g}_{\text{ads}}$ . Also, MIL-101(Cr) proved to be stable through 20 successive cycles at 25°C. The results from theoretical modeling of a two-bed adsorption system with heat and mass recovery have shown that using MIL-101(Cr)/ethanol pair has remarkable potential in low temperature cooling applications.

#### 2.4.3. MOFs-methanol pair

Jeremias et al. [46] showed that the use of alcohols (methanol) as working fluids turned be a good prospect for the application of otherwise promising, but hydrothermally unstable or



not sufficiently hydrophilic materials like HKUST-1 or MIL-101(Cr), respectively, or for low temperature applications, where the vapor pressure of  $H_2O$  is not sufficient for acceptable kinetics and that heat and mass transfer could be optimized by various shaping procedures.

### 3. Heat and mass transfer enhancements

Enhancing the heat and mass transfer (HMT) of the adsorber is the most crucial part in developing ARSs. For a given cooling capacity, higher specific cooling capacity (SCC) means smaller amount of adsorbent to be used, and that can be a direct result of improving the heat and mass transfer performance of the adsorber. Besides, a lighter weight and smaller volume are existed in such case. As the adsorption system consumes less heat during regeneration modes, the COP is increased. Two methods are commonly used to increase the HMT: one is the development of adsorbents and the second is the optimization of the adsorber designs and cycle modes.

#### 3.1. Adsorbent developments

Intensifying the heat transfer of an adsorbent depends mainly on increasing its thermal conductivity where the conduction is the major way to transfer the heat through the adsorbent. Consolidating the adsorbent or using additives with good thermal conductivity into the adsorbent are the common approaches used to enhance the heat transfer in the adsorbent [50, 51]. However, such approaches always decrease the permeability of the adsorbent leading to a decrease in inter-particle mass transfer. The overall performance of the bed will be affected by this contradiction between *heat transfer* and *mass transfer* in the adsorbent. Thus, it should be considered that the increase in thermal conductivity 20-fold, for example, does not mean a similar great enhancement in the overall performance due to the reduction in mass transfer. On microscopic level, the distribution of micro layers inside the samples of an adsorbent affects both the thermal conductivity and permeability, and then investigation can be applied for enhancing both of them as made in Ref. [52]. Therefore, sample preparation and filling techniques can be optimized to enhance both heat and mass transfer. Testing adsorbents in various forms and sizes is also an effective way to investigate the best HMT performance of the adsorber. Developments of the composite adsorbents are another active area used to enhance refrigerant uptake of the pure adsorbents and their stability. More recently, there are two trends: coating the adsorbent over the heat transfer metal surfaces of adsorbers, aiming at the elimination both of thermal contact resistances and large inter-particle voids, or using the new metal-organic frameworks (MOFs) materials which provide attractive adsorption characteristics compared to common adsorbents.

##### 3.1.1. Adsorbent coatings

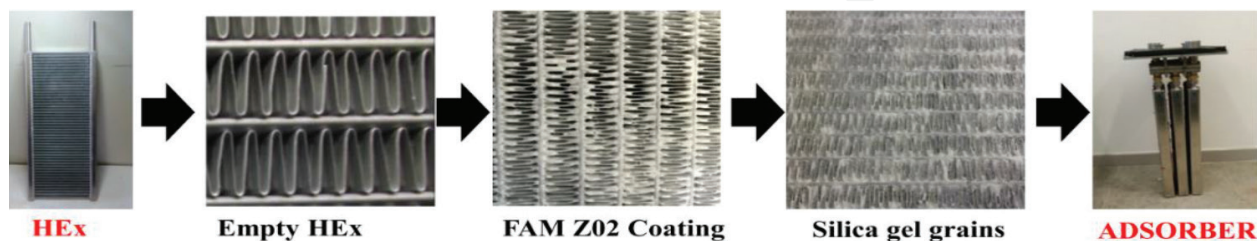
From the standpoint that loose grains and consolidated adsorbent beds have poor heat transfer and mass transfer properties, respectively, the concept of coated adsorber has been developed

to introduce adsorbers with efficient heat and mass transfer. Applying direct synthesis, or using a binder for deposition a layer of adsorbent over walls of the metal heat exchangers are two common technologies of adsorbent coatings. Different approaches have been reported and discussed in Ref.s [53, 54] as for illustrated in **Figure 8** [55].

### 3.2. Optimization of the adsorber design and cycle modes

Optimized parameters and sophisticated designs of adsorber configurations can help in enhancing the inter-particle mass transfer in the adsorbent domain, along with facilitating the heat transfer between the adsorbent and heat transfer fluid HTF. Extended metal surfaces 'fins' are commonly used to intensify the heat transfer and overcome the low thermal conductivity of the adsorbent materials. However, the COP of an adsorption system is strongly affected by the metal-adsorbent mass ratio [56]. Therefore, the net effects of the fins parameters such as fin spacing, height and thickness should be investigated carefully to optimize the overall system performance [57–60].

In the same context, operational control parameters, such as adsorber modes' durations and fluid flow rates, influence considerably the ARSs' performance and need to be also optimized. Basically, in view of the fact that the diffusion of mass within the adsorbent particles is better with higher temperatures, therefore, the desorption process is carried out faster than the adsorption process. That explains why the differences between equilibrium and instantaneous amount of adsorbate ( $W_{eq} - w$ ) in desorption and adsorption modes are not identical during the cyclic steady state. A larger difference is required during an adsorption mode to adsorb the same total amount desorbed during a desorption mode for making cyclic steady state. Increasing the cooling water velocity and/or adsorption duration over heating water velocity and/or desorption mode are the common ways to reach steady state cycle. And that increases need to be optimized for maximizing the adsorption system performance, as by adsorption/desorption times reallocation, [61]. Operating under low pressures is another challenge as in the case of water and methanol as refrigerants. In this case, the poor mass transfer in adsorbers can lessen greatly the difference in the refrigerant uptakes during the cycle. That requires more developed designs for such adsorbers to improve their performances. It is important to mention that studying the net effect of any operating parameter on the adsorption kinetic during only one mode (adsorption or desorption) based on given initial conditions may lead to inaccurate predictions for the overall performance.



**Figure 8.** Adsorbers' manufacturing procedure [55].

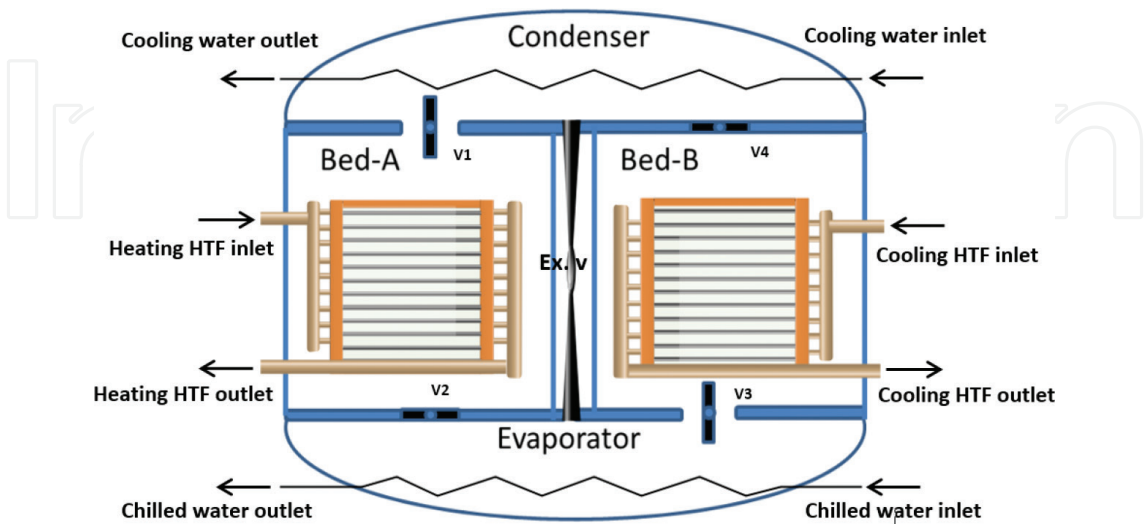
4. Advanced adsorption cycles

In view of the fact that the basic adsorption cycle produces intermediated cooling output and its COP is low, many advanced adsorption refrigeration cycles have been proposed and developed to help in overcoming these main drawbacks such as the heat recovery cycle, mass recovery cycle, thermal wave cycle, cascade cycle and multi-stage cycle. However, the basic cycle is mostly used in the solar powered adsorption system for its simplicity.

4.1. Two-bed adsorption cycles

The flow diagrams of a conventional two-bed cycle representing one complete cycle are illustrated in **Figure 9**. Each adsorber undergoes four operating modes: pre-heating, heating (desorption), pre-cooling and cooling (adsorption) processes in repeating cycles and according to the sequence shown in **Table 1**. The system consists of two adsorbent beds, a condenser, an evaporator and an expansion valve, in addition to the four connecting valves and connecting pipes. The working principle of the basic cycle is discussed in detail in Section 1.1 for one-bed ARS. In a two-bed ARS, while hot water is used to heat up Bed-A during the first two processes: cooling water is used to cool down Bed-B. The hot water is switched to Bed-B in the last two processes, as Bed-A is subjected to cooling water. The four valves are completely closed during the two switching modes. Circulating the cooling water and chilled water in the condenser and evaporator, respectively, are supposed to be continuous during the whole cycle.

In a system of two or more adsorbers work between an evaporator and a condenser, there is a hot adsorber under cooling process and a cold one under heating process which offers the availability to recovery the heat inside the system. The experimental results show that the COP of the system will increase by up to 25% with the heat recovery cycle [62]. In a

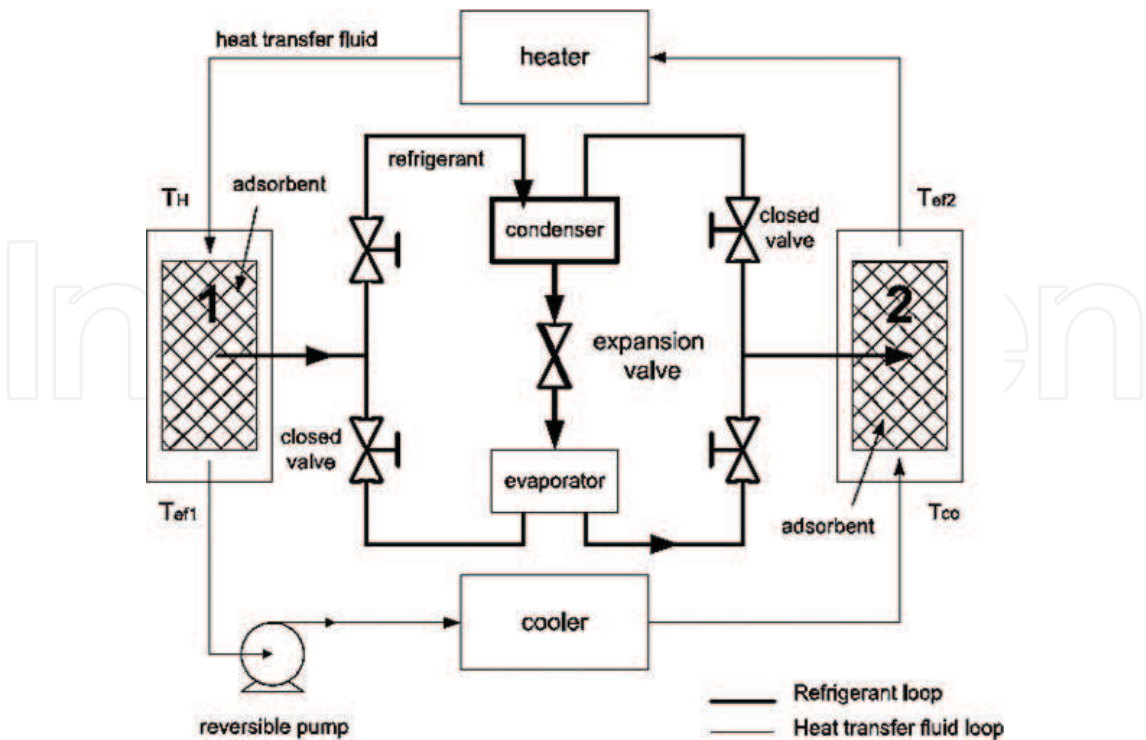


**Figure 9.** Schematic diagram of a conventional two-bed adsorption chiller, as Bed-A in desorption mode, Bed-B in adsorption mode.

Mode	Component					
	Bed-A	Bed-B	V1	V2	V3	V4
Mode-A switching	Pre-heating	Pre-cooling	X	X	X	X
Mode-B Des/Ads	Heating/Des	Cooling/Ads	O	X	O	X
Mode-C switching	Pre-cooling	Pre-heating	X	X	X	X
Mode-D Ads/Des	Cooling/Ads	Heating/Des	X	O	X	O

**Table 1.** Cycle modes and valve positioning.

typical two-bed cycle equipped with mass recovery system, while one bed at the end of desorption mode at higher pressure and temperature, the other bed at the end of adsorption mode at lower pressure and temperature. Internal mass recovery process is started via connecting the high-pressure adsorber to the low-pressure one typically by means of a valve. The process ends when the two pressures become equal. The combined heat and mass recovery procedures may increase COP more than 10% [62], compared to heat recovery cycle. Thermal wave cycle is another way to recover the heat inside the cycle. A typical thermal wave cycle is composed of two adsorbers, an evaporator, a condenser, a cooler and a heater as shown in **Figure 10** [63]. Experimental results showed that the COP of a two-bed adsorption air conditioner (zeolite-water) with thermal wave cycle was approximately 1.0 in cooling season [12].



**Figure 10.** Schematic representation of the thermal wave adsorption heat pump during the first half of the cycle [63].



An adsorption chiller installed in the University hospital in Freiburg [64]

Working pair: silica gel-water  
CC(kW): 70 and COP –  
Backup: thermally driven by steam network of the hospital  
Daily solar radiation: temperate, central European climate  
Solar collector type: evacuated tube  
Area: 170 (m<sup>2</sup>)  
Main features: solar system is working on assisting the main driving heat system and can deliver about 90% of the heating required in mid-day hours (4 hours)



Adsorption chiller installed in the University hospital in Freiburg

Two-bed adsorption chiller developed by SorTech [65]

Working pair: silica gel-water  
CC (kW): 7.5 and COP: 0.55 (system)  
Electricity consumption: 9 W.  
Heat supply circuit: 72/67°C at 1.6 m<sup>3</sup>/h. Heat rejection circuit 27/32°C at 3.7 m<sup>3</sup>/h. Chilled water circuit 18/15°C at 2.0 m<sup>3</sup>/h.  
Daily solar radiation: temperate, central European climate  
Solar collector type: flat plate  
Area: 3.5–4.5 (m<sup>2</sup>/kW)  
Main features: developed by SorTech AG, and it enables to paste the heat exchanger surface with silica gel pellets with the aid of epoxy resin without blocking the entrance pores of the pellets



The Fraunhofer ISE institute building and SorTech adsorption chiller in the technical room (sources: Fraunhofer ISE) [34]

Silica gel-water adsorption chiller developed in SJTU [66]

Working pair: silica gel-water  
CC(kW): 15  
COP: 0.35 (system) 0.15 (solar)  
Regeneration temp. (°C): 85  
Solar collector type and area: 90 m<sup>2</sup> of U-type evacuated tube and 60 m<sup>2</sup> of heat pipe evacuated tubular  
Main features: the adsorber is a compact finned-tube heat exchanger, the condenser is a shell and tube heat exchanger, and the evaporator cooling is output through a methanol chamber, which acts as a gravity heat pipe. Power consumption for pumps was 1.87 kW



Photo of the adsorption chiller

**Table 2.** Summary of some adsorption prototypes.

## 4.2. Other advanced cycles

There are many of advanced and novel cycles proposed in literature for ARSs. The advanced cycles such as multi-bed cycle, multi-stage cycle and dual-mode cycle are originally developed to make utilize of lower temperature heat sources applicable and more efficient. Another trend in advanced cycles is eliminating the vacuum valves by putting the adsorber, condenser and evaporator in a single chamber to increase the reliability of the system, particularly under the vacuum operating conditions. **Table 2** summarizes data about some applied or prototype adsorption chillers.

## 5. Conclusions

Adsorption refrigeration systems have a lot of advantages making them more and more competitive when compared to conventional vapor compression refrigeration systems. Apparently, the environmental regulations and local safety considerations, the expensive and limited petrol energy resources, solar driven possibility and the increasing of industrial waste heat availability are all in favor of thermally driven refrigeration systems, particularly adsorption systems. The adsorption refrigeration technology has not been carrying out in mass production level yet. That justifies its higher initial cost compared to the conventional technology. On the other side, there is a serious need to consider together all aspects of energy, exergy, environment and economy in the future comparative studies. Also, it should be noticed that the thermal COPs of ARSs are around 0.6 which is low. However, the electrical COP values of ARSs can reach up to 10 which is high compared to that values of conventional systems typically between 3 and 5. In order to find out new direction of adsorption refrigeration systems developments, previous related researches are reviewed and classified in this chapter.

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## Nomenclatures

ARSs	adsorption refrigeration systems
COP	coefficient of performance
HEX	heat exchangers



MOFs	metal-organic frameworks
SCC	specific cooling capacity
$W_{eq}$	equilibrium amount of adsorbate

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