An Overview of Developments in Adsorption Refrigeration Systems: Principle and Optimization Techniques

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Abstract: The Negative environmental impacts and limited sources of fossil fuels are the major reason to focus on renewable energy sources, predominantly solar energy. Refrigeration and air-Conditioning processes consumes fifteen percent of the electricity produced in the whole world. Environment friendly adsorption cooling systems are possible alternatives to conventional electricity-driven vapour compression refrigeration systems. Comparatively bigger sizes of adsorption based cooling units, due to their low specific cooling power & manufacturing cost, are major roots that preventing successful commercialization of the technology. Efforts are on, to enhance the performance of adsorption systems through improvements in working pair's properties, improved heat and mas transfer by efficient design of adsorbent bed. This paper traces the basic principle, improvement techniques & analyses the barriers to wide spread use of adsorption refrigerators.

Keywords: Adsorbate, Adsorbent, Renewable energy, Working pairs, Solar energy.

Introduction

The standard of living of people are increasing drastically, and proportionally day by day, demand of cooling ,comfort air conditioning and refrigeration are increasing. Orthodox cooling technologies are generally electricity driven customary vapor compression refrigeration systems which usually operated with synthetic refrigerants [1], such as CFCs, HCFCs or HFCs, they causes the ozone layer depletion and/or cause greenhouse effect. As a result, several protocols, like the Montreal Protocol (1987) or the Kyoto Protocol (1997), were established in order to considerably reduce, the emissions of these refrigerants [3, 4]. However ,the situation continue demanding for the development of alternative technologies operating with environmentally friendly substances, especially due to the increasing emissions of HFCs, although the emission of CFCs and HCFs have been decreasing since the late 1980s [5,6]. Furthermore, the ever increasing energy consumption worldwide makes it urgent to find new ways to use the energy resources in a more efficient and rational way. It is estimated that the global energy consumption will increase by 71% between 2003 and 2030 [7]. In addition, currently 80% of the energy on Earth comes from fossil fuel resources [8].

Usual vapor compression refrigeration cycles are electrically powered, which leads to fossil energy consumption; and also largely contributing to the greenhouse effect. In another perspective, a considerable percentage of the world population is in remote areas, where the electricity supply is rare deficient or even non-existent, The need for refrigeration systems in these locations is of extreme importance since ,due to the electricity shortage, conventional refrigeration equipment cannot be used ,for instance ,in food and medicines storage ,Ice making or even for air-conditioning. Therefore ,the awareness on issues such as the decrease of fossil fuel resources, the severe environmental problems or even the location challenges (e.g., remote areas) require the development of new technologies and led the human kind to look with greater interest for ecological and renewable energy sources. These include wind, solar, hydropower biomass and geothermal energies, or even thermal waste from various processes.

Solar energy currently a subject of great interest, and refrigeration is a particularly attractive application due to the coincidence between the peak of cooling demand and the solar radiation availability. Recently, adsorption refrigeration processes have been investigated (theoretically and experimentally)and proposed as an alternative to vapor compression refrigeration systems ,attempting to preserve the production and efficiency level of traditional systems, and becoming one of the most promising solar refrigeration methods [4]. Adsorption systems are not cost-competitive, and have some technical drawbacks, such as low coefficients of performance (COP),low specific cooling powers(SCP),and poor heat and mass transfer on the adsorbent beds ,which makes the systems more bulky and expensive [10,11]. Moreover, in the case of solar refrigerators, the energy source is intermittent and can also be highly irregular. However, these systems promote significant primary energy savings in comparison with common mechanical vapor compression refrigeration systems, and have simpler control, no vibration, no noise, lower operation and maintenance costs, lower environmental impact, and are simpler and more robust [11]. Compared with the absorption systems, adsorption systems can be powered over a large range of heat source temperatures, are more robust and less sensitive to physical impacts ,do not present corrosion problems ,and are less complex because they contain fewer moving parts[11,12].Therefore, the adsorption refrigeration systems appear as a good alternative to replace(or integrate)the traditional refrigeration systems by more environmentally friendly systems ,which can be powered by renewable energy sources. Researchers worldwide are working to improve the performance of adsorption cooling systems in order to overcome its current technical and economic issues.

The process

Principles of adsorption

The adsorption is a surface phenomenon, which result from the interaction between a solid and a fluid (refrigerant) based on a physical or chemical reaction. Physical adsorption occurs when the molecules of refrigerant (adsorbate) fix themselves at the surface of a porous solid element (adsorbent), which is due to Vander Waals forces and electrostatic forces. By applying heat, this process can be reversed in which adsorbate molecules can be released (Which is called desorption process).In turn, the chemical adsorption results from the ionic or covalent bonds formed between the adsorbate molecules and the solid substance. The bonding forces are much greater than that of physical adsorption, releasing more heat. However ,the process cannot be easily reversed .Besides, this type of bonding promotes the chemical alteration of the adsorbed substance ,thus the adsorbate and adsorbent molecules never keep their original state after adsorption .Therefore, most of the adsorption refrigeration systems mainly involve physical adsorption [12,14].These cycle leads to intermittent operation ,with the adsorbent bed alternating between the adsorption and desorption stages. Thus, when continuous cooling effect is required, two or more adsorbent beds must be operating out of phase, which require that heat source is always available, which is not the case of solar radiation.

Applications of the Adsorption process

- Solid adsorbents, in combination with suitable adsorbate can be used in air separation systems to separate gases,
- The principle of adsorption is used in refrigeration cycles to provide air-conditioning or for ice-making purposes. Several companies have successfully commercialized adsorption chillers,
- Desiccants such as silica gel and zeolite are also used in many systems to extract moisture from the air and prevent damage to products such as medicines, shoes, etc.
- Chemical Plant Uses;CO_2 removal from ammonia synthesis gas,CO_2 removal from H_2/CO mixture,NO_x removal from Gases,
- CO_2 and water removal from air in air separation plants.

Basic solar adsorption refrigeration cycle

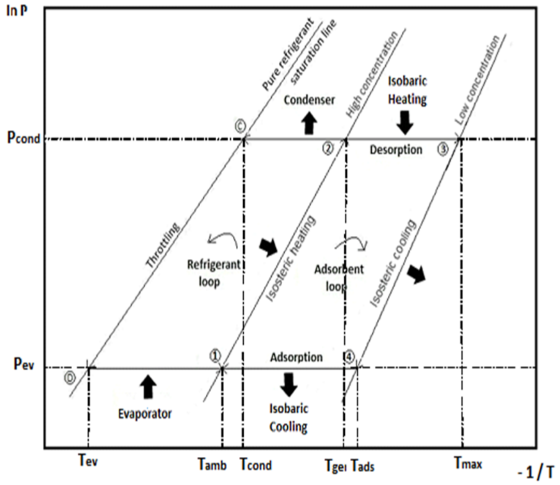

Fig.1. Theoretical adsorption cooling cycle indicating,
Phase 1: Isosteric heating (Process 1-2)
Phase 2: Isobaric desorption (2-3)
and condensation (2-C)
Phase 3: Isosteric cooling (3-4)
and throttling (C-D)
Phase 4: Isobaric cooling (4-1)
and Evaporation (D-1)

Selection of the working pair

Since the performance of the system greatly depends upon chosen working pair, choice should be made carefully The proper selection depends on the temperature of the heat source ,the desired characteristics of the refrigeration system, the properties of the working pair constituents and the affinity between them(which depend on the chemical , physical and thermodynamic properties of the substances),and also on their cost ,availability and environmental impact.

Choice of adsorbent

The most important features for choosing a suitable adsorbent are [13, 17]:
-Ability to adsorb a large amount of adsorbate when cooled to ambient temperature,
-Desorption of most (ideally all) of the adsorbate when heated by the available heat source,
-Higher apparent density; high pore volume; high surface area,
-Low specific heat; Good thermal conductivity, to shorten the cycle time; High porosity (in the order of 600 m^2/g)
-Chemically and physically compatible with the chosen refrigerant; Non-toxic and noncorrosive; Low cost and wide availability.

While selection there must be compromise between the high porosity required for rapid vapor diffusion and the high density required for good thermal conductivity [20]. The most commonly used adsorbents are activated carbon, zeolite and silica-gel .Activated carbon offers a good compromise between high adsorption and desorption capacities. Natural zeolites need to be present in large quantities since only a small amount of adsorb ate is desorbed during the temperature increase. However, the adsorption isotherms of zeolites have extremely non-linear pressure dependence, which is relevant for solar refrigeration applications .Contrarily, activated carbon and silica-gel present almost linear pressure-dependent isotherms. Silica-gel satisfies most of the criteria listed above but it is expensive and may not be available in most countries. Besides, the deterioration phenomenon of the adsorption capacity and aging of silica-gel is another current issue [13, 18, and 21].

Improvement in adsorbent

Basic adsorbent can we doped to present better performance when applied in adsorption refrigeration.Gordeeva et al. [31] presented new family of methanol sorbents ”salts in mesoporous silica” in adsorptive air conditioning system. They concluded that these synthesized composite sorbent has a higher adsorption capacity. Composite Licl/sio2 shows the highest sorption capacity Wads = 0.8 g/g.Tso et al [32] carried out study on composite adsorbent that were synthesized from activated carbon, silica gel and cacl2.Their result showed that the maximum adsorption capacity of 0.23 kg 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 0.02 kg water /kg adsorbent at the same conditions. Wang et al [33] studied a specially treated activated carbon fiber and concluded that it might be a good substitute as refrigeration capacity and adsorption time are 3 times more and 1/5 to 1/10 of those normal AC, respectively .Other technique is to use consolidated adsorbents to increase the thermal conductivity. Which increase the density and thermal conductivity by 20% and 145-209 % respectively.

Choice of adsorbate

The adsorbate or refrigerant must fulfill the following requirements [9, 17]:
-Evaporation temperature below 0 degree C (for refrigeration purposes; it can be higher in the case of air conditioning applications); Small molecular size so as to facilitate the adsorption effect;
-High latent heat of vaporization and low specific volume when in the liquid state; High thermal conductivity; Low viscosity.
-Thermally stable with the adsorbent in the operating temperature range; chemically stable in the operating temperature range;
-Non-toxic, non-corrosive and non-flammable
-Low saturation pressures (between 1 to 5 atm) at normal operating temperature; Absence of ecological issues, unlike common refrigerants.

The most commonly used refrigerants are ammonia, methanol and water, which have relatively high latent heat values (1368, 1160 and 2258kJ/kg, respectively) and low specific volumes (of the order of 0.001 m3/kg). Water and methanol operate at sub-atmospheric saturation pressures at the operating temperatures. In the case of ammonia, it operates at higher pressures so small leakages can be tolerated in some cases; Ammonia is an example of positive refrigerant. Ammonia is toxic and corrosive, while water and methanol are not, but the second is flammable .Water is the most thermally stable adsorbate, closely followed by methanol and ammonia, in that order .However, water cannot be used for cooling purposes below 0 ˚C [18].

Review of working pairs

There are some observations regarding adsorbent–adsorbate working pairs for adsorption refrigeration system. The most commonly used working pairs are: zeolite-water, silica gel– water, activated carbon-methanol and activated carbon-ammonia [9]. Silica gel–water is ideal due to its low regeneration temperature; require low grade heat sources, commonly below 85 degree C. Moreover, water has the advantage of having a greater latent heat than other conventional refrigerants. It is suitable for air- conditioning application .(It is widely used in adsorption chillers).However, this pair has a low adsorption capacity as well as low vapor pressure ,which can hinder mass transfer .Furthermore ,this working pair requires vacuum conditions in the system ,where by any non-condensable gas will cause a significant reduction in the systems performance [5,25,27,28]. Activated carbon-methanol is one of the most common working pairs in adsorption refrigeration systems. It also operates at low regeneration temperatures (care must be taken since regeneration temperatures above 120˚ C promote the decomposition of methanol), while its adsorption-evaporation temperature lift is limited to 40 degree C. This pair is also characterized by its large cyclic adsorption capacity, low adsorption heat, low freezing point and high evaporation latent heat of methanol .However, activated carbon has a low thermal conductivity, acting like a thermal insulator and causing a decrease in the system's COP, and activated carbon–methanol also operates at vacuum conditions. Besides, methanol must be used with caution due to its high toxicity and flammability [15, 27, 29]. Sequentially, the activated carbon–ammonia pair requires regeneration temperatures that can exceed 150 ˚ C. Its adsorption heat is similar to that of the pair activated carbon–methanol, but it requires higher operating pressures(about 1600 kPa),which enhances the heat and mass transfer performance and reduces the cycle time, also preventing the infiltration of air into the system. All these factors help to increase the specific cooling capacity of the system. Moreover, this pair suitability to high temperature energy sources and the high cooling capacity of ammonia.However,the activated carbon has a lower adsorption capacity with ammonia than with methanol; furthermore, care must be taken due to the ammonia toxicity, irritating odor(even at low concentrations)and corrosive nature [4,26]. For the zeolite–water pair, the regeneration temperatures can go beyond 200˚ C, with an adsorption-evaporation temperature lift up to 70˚ C or more. This pair remains stable at high temperatures, and the water latent heat is much higher than that of methanol or other traditional refrigerants. However, a system operating with the zeolite-water pair is more fitted for air-conditioning applications due to the solidification temperature of water, which restrains the freezing process. Other disadvantages of this pair are the low adsorption quantity, which is about 0.2kg/kg. Anyanwu and Ogueke [29] evaluated the thermodynamic performance of different working pairs when designing a solar adsorption refrigerator .It was concluded that the activated carbon–ammonia pair presents the best results for ice making, deep freezing and food conservation applications. In turn, the zeolite–water pair is better suited for air-conditioning applications. Because the lowest evaporating temperature of water is 0 degree, and due to its high latent heat of vaporization, suitable for producing chilled water, it is a proper choice for air-conditioning purposes. The activated carbon–methanol pair is also suitable for ice production and freezing applications [3].

Improvement in conventional pair

Habib et al. [33] investigated three pairs of adsorbent/adsorbate according to Malaysia climate conditions. The selected pairs were activated carbon-methanol; A.C fiber ethanol, silica gel water, among them amount of adsorbate, adsorbed/desorbed was highest for A.C fiber ethanol and then for A.C/methanol and the lowest was for the silica gel/water. Simulations for the six working pairs [ACF (A-15)/ethanol, ACF (A-20)/ethanol, silica gel/water, Chemviron/R134a, Fluka/R134a and Maxsorb II/R134a] are carried out at partial vacuum and pressurized conditions. By loh et al. Among these working pairs, Maxsorb II/R134a has the highest uptake capacity about 0.36 kg/kg which is followed, respectively by ACF (A-20)/ethanol, ACF (A-15)/ethanol, Fluka/R134a, silica gel/water and Chemviron/R134a pairs. [34].El-sharkawy et al. [35] studied that Maxsorb III/methanol pair has superiority among other carbonaceous adsorbent/methanol pair for both A.C & Ice making. They concluded that adsorption capacity 1.76 times than that of activated charcoal/methanol. Allouhi et al [36] observed the optimal performance for 7 pairs of adsorbent/adsorbate (A.C fiber/methanol, A.C/methanol, A.C/ethanol, silica gel/water, zeolite/ethanol, and zeolite/water) according to Moroccan city fez, morocco. The maximum uptake was obtained by A.C fiber/methanol (0.3406 kg/kg) whereas the maximum SCOP was about 0.384 for silica gel/water.

Optimization of structure

To achieve the high performance of adsorbent bed, one of the method is to expedite the pass of the heat absorbed by bed to adsorbent for desorption of the adsorbate by improving the heat transfer structure of bed .second one is to enlarge the mass transfer channels in the adsorbent bed to make the desorbed adsorbate get into condenser quickly, for that bed pressure should remain steady in favorable to more adsorbate desorption. Another method is to reduce heat loss by improving thermal insulation. Xu ji et al. [37] has developed an enhanced heat and mass transfer finned tube casing. Comparing with the metal casing with the same dimension, finned tube has 51.4 % more heat transfer per unit length. The aluminum alloy was used to build the casing due to its high thermal conductivity, low specific heat. Also, some experiments corresponding to the adsorption/desorption process with and without valve control were implemented. The cooling efficiency with control valve is higher than that without valve control.

A majority of analysis are developed by using evacuated tube or flat plate collector, whereas less attention has been given to PTCs. Abu-Hamdeh et al. [38] has developed model which uses parabolic trough solar collector to improve its overall performance and productivity .It uses olive waste (as an adsorbent) with an methanol (as an adsorbate).They obtained optimum adsorbent mass, tank volume, collector area .but it require sun tracking system.

Table 1. Some typical research group on adsorption refrigeration system

Research Group	**Application**	**Pair**	**Source Temperature Or Solar radiation**	**Arrangement**	**Ice mass per day**	**COP**	**Remarks**
Li et al.[40]	Ice making	A.C-Methanol	100° to 130° C	Flat plate collector	4-5 kg	0.12-0.14	Temp. of ice reached to -1° C
N.M.Khattab [41]	Ice making	Charcoal-Methanol	120° to 130° C	FPC with side reflector	6.9-9.4 kg/m^2	0.136 -0.159	Granular dia. 5-7 mm Porosity-46.45%
Z.Taminot-Telto[42]	Ice making	A.C-NH3	90° to 120° C	Heating coil and boiler	SCP : 60 W/kg	0.12	Evaporation T up to -20°C
Boubakri et al.[43]	Ice making	A.C-Methanol	19-29 MJ/m^2	FPC	5-11.5 kg/m^2	0.33 - 0.36	Collector Condenser mechanism
Abu-Hamdeh et al.[44]	Chilled water/A.C	Olive waste-methanol	95 to 120° C	Parabolic trough solar collector	-	0.75	Best cooling adsorbent mass: 30-40 kg, Collector area : 3.5-5 m^2
Xu ji et al.[45]	Ice making	A.C-Methanol	11-20 MJ/m^2	FPC with finned tube casing	6.5 Kg	0.039 - 0.122	Under a typical weather condition
Saha et al.[46]	Chilled Water	Silicagel-Water	55-75° C	Hot water supply	3.2 KW	0.36	Two stage adsorption chiller, Properties are given
Wang et al.[47]	Chilled Water	A.C-Methanol	80 -110° C	Waste heat driven	2.6 kg/kg &SCP 150 W/kg	0.4	Dual refrigeration & A.C
W.Wang et al.[48]	Review paper	Activated carbon & ACF	-	-	-	-	ACF provide better surface area and better mass transfer.

The adsorption refrigeration tube (ART) has drawn increasing attention because of its advantages of no moving parts, compact structure. Zhao et al. [39] has developed a new design of ART, in which activated carbon–methanol was selected as the working pair for either refrigeration or air-conditioning purposes. They employed condenser, evaporator and generator in a single tube. A concept of transient boundary i.e. transient pressure (and transient vapor density) was introduced for the first time into the model.

Conclusion

Low specific cooling power of the system leading to bigger sizes of the chillers and comparatively higher investment cost are major causes to prevent successful commercialization of the technology. It still needs a lot of research on adsorbent materials, improved heat and mass transfer, advanced cycles, etc. to make this technology a competitive one.

This work will help to understand basic phenomenon of ARS as well as selection criteria to select suitable pair according to application. In our opinion, the adsorption technology would direct towards development of Ecofriendly green technology for refrigeration purpose in remote areas.

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