ABSTRACT

Solar adsorption refrigeration devices are significant to meet the needs for cooling requirements such as air-conditioning, ice-making and medical or food preservation in remote areas. They are also noiseless, non-corrosive and environmentally friendly. Various solar powered cooling systems have been tested extensively; these systems are not yet ready to compete with the well-known vapor compression systems. For these reasons, research activities in this sector are still on to solve the technical, economical and environmental problems. So, the primary objective of this work is to provide fundamental understandings of the solar adsorption systems and to give useful guidelines regarding the working principles of the various intermittent adsorption systems and their applications in ice-making with the aim of improving Coefficient of Performance (COP). Also, in this work, a review of the research state of art of the solar sorption (absorption and adsorption) refrigeration technologies is presented. After an explanation of the systems working principles, recent progress in solar sorption refrigeration technologies are also reported. It shows that solar-powered sorption systems refrigeration technologies are attractive alternatives that not only can serve the needs for air-conditioning, refrigeration, ice-making and cooling purposes, but also can meet demands for energy conservation and environmental protection.

KEYWORDS: Adsorption, Adsorbate, Adsorbent, Zeolite, Ice-Making

1. INTRODUCTION

In the early years of the century, Sorption Technology was frequently used, later, with the development of cheap reliable compressors and electric motors, the improvement on power station efficiency and the CFCs in the 1980s, it then became a forgotten technology (Anyawu, 2009, P. 301-307).

However, recent years have witnessed increasing interest in this technology for many different reasons. The main arguments in favor is that sorption systems are quiet, long lasting, cheap to maintain and environmentally friendly. Before the technology is explained, there's the need for the general sorption systems to be discussed (which are the Absorption Technology and the Adsorption Technology; both important for ice making). The existing systems for producing cold, using solar thermal energy are based mainly on the phenomena of sorption; the process by absorption liquid-gas and the process by adsorption solid-gas (Best, Ortega, 2006, P. 687). The adsorption process concerns separation of a substance from one phase, accompanied by its accumulation or concentration on the surface of another. On the other hand, absorption is the process in which material is transferred.
from one phase to another, and interpenetrates the second phase to form a solution. Solar refrigeration is a useful application of solar energy in areas of the world where there is a demand for cooling and high insolation (Boubakri, 2003, P.832) levels, and no firm electricity to supply conventional power systems. One of the very effective forms of solar refrigeration is the production of ice, since ice accumulates much latent heat in it. Although different adsorption pairs had been studied to build adapted solar ice maker, the activated carbon– methanol pair was found the most suitable for solar-powered refrigeration since it could be driven by heat of relatively low temperatures. Also it is less expensive than other pairs. The adsorption solar refrigerator in its simplest form is a closed system composed of the container of adsorbents and adsorbate (sorption bed), which serves as a solar collector, a condenser and an evaporator. The cycle of this system is divided into two periods: First, the adsorbent is heated by solar energy during the day and the desorbed adsorbate is condensed. Then the adsorbent is cooled after sunset, thereby re-adsorbing the adsorbate, the evaporation of which produces the refrigeration effect. As desorption is highly endothermic, the heat input to the adsorber must be large enough to allow for sufficient refrigerant to be desorbed. On the other hand, (Cotsman, Chritoph, 2008, P.708) adsorption is highly exothermal, so, cooling down of the adsorber is also a major concern. Although, the alternation of heating and cooling during the cycle perfectly suits the intermittent nature of solar energy, yet efficient operation of the system requires high rates of heat transfer in and out of the adsorbent. Unfortunately, some problems are encountered which affect rates of heat transfer. First, the heat transfer of adsorbent bed in most current prototype is very poor, due to low convective heat transfer to the adsorber and bad thermal conductivity of the adsorbent. Second, the thermal mass of the container presented an unacceptably high thermal load which affected alternation of heating and cooling. Third, the system suffers from the problem of being tightly sealed against air leakage through the joints and valves which results in degrading the cooling performance.

1.1 Absorption
Absorption systems originally direct fired, operated with steam and hot water are now designed to operate with natural gas, biogas town gas, waste heat from industry and solar energy. Although, the market is still dominated by single stage absorption chillers, double effect have been produced for many years. The system(absorption refrigeration) is based
on the principle that some absorbents can absorb large quantities of refrigerants which can be regenerated upon the application of heat. The refrigerant absorption process is exothermic, while the regeneration process is endothermic. The heat energy required for the regeneration process may be supplied from any suitable heat sources, such as waste heat from a heat engine or process plant heat from a compression system, bio-fuels or solar energy. There are two types of absorption systems, which are the LIQUID ABSORPTION SYSTEM and the SOLID ADSORPTION SYSTEM.

1.1.1 Liquid absorption systems: following the pioneer work of Enibe and Anyanwu, who built and tested a water/ammonia solar refrigerator, many reports on the performance of Solid and Liquid Absorption Systems have appeared in the literature. Critoph constructed an intermittent water/ammonia plant with three glazing covers which produced 1.43kg of ice per m² a day. Other intermittent systems based on water/ammonia and NaSCN/NH₃ are reported by Guang Dong and these gave Coefficiece of Performance in the range 0.05-0.14. A continuous water/ammonia plant which used two pumps for the absorbing solution and chiller water is reported by Floride (Critoph, 1996, P.430) in 1986. The system was single glazed with 1.49 m² collector area and gave a coefficient of performance(COP) of 0.1 and an ice production capacity of 12.5kg per meter square per day.

1.1.2 Solid absorption system: In comparison with the liquid absorption systems, relatively fewer solid absorption plants have been reported. In 1959, in Germany, Planks activated carbon - ammonia system used 100% hot walls as heat source, had a cooling capacity of 3768-4187kj/cycle and gave 3 cycles per day, but before this, in 1951, in Liverpool, Andrew’s (Critoph,1996) activated carbon – ammonia plant also used 100% steam as hot source, and operated commercially on refrigerated food transport vans on London to Liverpool trains during the second world war. In 1969, in Russia, Murador and Shadier also built a NaCl₂/NH₃ system which produced 1kg of ice per m² per day, while in 1975, Eggers- Lura et al designed a plant capable of producing 4.6kg of ice per day with CaCl₂ or FrCl₂ as absorbents and NH₃ as refrigerant. In 1985, Iloeje built an intermittent CaCl₂/NH₃ system with a double glazed collector of 1.41m² surface area. This gave cooling capacity of 714kj/m² with an effective ice production of 1.5kg per meter square per day.
1.1 Adsorption
Adsorption is the general phenomenon resulting from the interaction between a solid (adsorbent) and a gas (refrigerant) based on a physical or chemical reaction process. An adsorption refrigeration machine utilizes the phenomenon of physical adsorption to be fixed at the surface of adsorbent through connections of the Van der Waals forces. Adsorption process can be classified as either physical or chemical, depending on the forces causing the adsorption process. Physical adsorption (physisorption) occurs when Van der Waals forces bind the adsorbing molecules to the solid phase, these intermolecular forces are as same as ones that bond molecules to the surface of a liquid. The chemical adsorption (chemisorption) occurs when covalent or ionic bonds are formed between the adsorbing molecules and the solid substance. Adsorption is an endothermic process accompanied by evolution of heat, the quantity of heat released depends upon the magnitude of the electrostatic forces involved, latent heat, electrostatic and chemical bond energies. The heat of adsorption is usually 30-100% higher than the heat of condensation of the absorbate. In 1972, the theory of adsorption was extensively discussed in New York by Levenspiel. It proffers that during adsorption, a molecular species of a fluid is attached to the surface of a solid, resulting in an increased concentration of the substances at the interface. Of the various adsorbent/refrigerant pairs tested by Critoph in 1986, R22 with activated charcoal appeared to be the best, with a maximum COP estimated at about half that of the ammonia/water system. More recently, however, in 2008, Guang Dong (Dieng, Wang, 2001, P.313-315) built an activated carbon refrigerator using ammonia as refrigerant. The collector has an area of 1.4 meter square and contained 17kg of active carbon. Under simulated radiation conditions in the laboratory, the unit gave an equivalent COP of 0.05-0.09, with a cooling capacity of 511-1007kj/m² per day. Ethanol has also been investigated as a possible refrigerant, with activated charcoal as the adsorbent. According to the information gathered from past works, much research has been performed on sorption refrigeration. In this work, most attention will be focused on the intermittent cycles due to the limiting conditions imposed by the use of solar adsorption.

2. Refrigerants and Adsorbents
These are several working pairs for solid adsorption. For the successful operation of a solid adsorption system, careful selection of the working medium is essential. It is
because the performance of the system varies over a wide range using different working pairs at different temperatures. For any refrigerating application, the adsorbent must have high adsorptive capacity at ambient temperatures and low pressures, but less adsorptive capacity at high temperatures and pressures. Also, the refrigerant is one of the most important elements of any heat pump or refrigeration system, since the working pair conditions and compatibility with the environment is practically on it, and, the refrigerant requirements high latent heat per units volume and good thermal stability. Briefly, adsorption characteristics of adsorbent are determined by the adsorption isotherms, for the amount of substances adsorbed.

In 1981, Tchernev (Enibe,1997, P.158) carried out an investigation of adsorption refrigeration with zeolite/water pair. Also, in 1982, Pon et al worked on the adsorption pair, zeolite and water to produce refrigerating effect, achieving a COP of only about 0.1. Later in 1987, in France, Pons and Crenier demonstrated that activated carbon and methanol can serve as a suitable pair for a solar powered, solid adsorption ice-maker. In the year 2001, Critoph(Enibe,Iloeje,2006, P.435) studied the performance limitations of adsorption cycles with different adsorbents, for solar cooling and concluded that, in general, activated carbon/methanol combination was most preferable for solar cooling; giving the best COP achievable in a single stage cycle. In China, several studies had been carried out on solar powered refrigerators using different adsorption pairs such as zeolite/water and activated carbon/methanol

2.1 Choice of pairs
At present, three types of working adsorbate and adsorbent, respectively are favored for pairing for use in solid adsorption solar refrigeration technology: ammonia, methanol and water for adsorbate and activated carbon, silica-gel and zeolite for adsorbent. The selection of any pair of adsorbent/adsorbate depends on certain desirable characteristics of their constituents, including the affinity for each of other. These characteristics range from their thermodynamics and chemical properties to their physical properties and even to their costs or availability (Fan,Luo,2006).

2.1.1 Choice of adsorbate
The adsorbate for the application being investigated would have the following positive attributes;

1) Evaporation temperature below zero degree celcius.
2) Small size of molecules such that it can easily be adsorbed into the adsorbent.
3) Micropores of diameter less than 20Å.
4) High latent heat of vaporization and low specific volume.
5) Thermally stable with the adsorbent at the cycle operating temperature ranges.
6) Non-toxic, non-corrosive and non-flammable.
7) Low saturation pressures (slightly above atmosphere) at normal temperature (Florides, Tasson, 2002, P.45).

A survey of the favored working adsorbates shows that methanol and water operate at sub-atmospheric saturation pressures at the operating temperatures needed, and an ingress of air immediately results in system malfunction. Ammonia does not have this problem because its outward leak could be tolerated for some time, but its saturation pressure of 13 bar at 35°C condensing temperature is quite high. In the case of methanol, with a normal boiling temperature of 65°C, the low saturation pressures could be exploited advantageously to detect leakages, since it must necessarily result in abnormal increases in system pressure and poor performances. Ammonia, methanol and water, all have relatively high latent heat values of 1368,1102 and 2258 kJ/kg, respectively, and their specific volumes are low, on the order of about $10^{-3}$ m$^3$/kg. Ammonia is toxic and corrosive, while water and methanol are not, but the problem with alcohols is that they are flammable. Water is the most thermally stable adsorbent, closely followed by methanol and ammonia, in that order. However, water cannot be used for freezing purposes because its freezing temperature is 0°C. This makes methanol a favored adsorbate for pairing with a stable adsorbent.

2.1.2 Choice of adsorbent.

- The important considerations influencing the choice of a suitable adsorbent are;
- Adsorption of large amounts of the adsorbate under low temperature
- Conditions to yield a good COP.
- Desorption of most of the adsorbate when exposed to thermal energy.
- Possession of high latent heat of adsorption compared to its sensible heating load.
- Non toxic and non corrosive.
- Low cost and widely available.

Properties (1) and (2) tend to be mutually exclusive, although activated carbon strikes the best compromise of the adsorbents, discussed in the literature. Natural zeolites also have possibilities, but significantly larger quantities would
be required for, was as the adsorbate since only a modest amount of adsorbate is desorbed in going from room temperature to flat plate solar collector (Ghadar, Shihab, 1999, P. 540) temperatures. However, zeolites have another unique property in that their adsorption isotherms have extremely non-linear pressure dependence, which is of importance in solar refrigeration applications. Activated carbon and silica-gel have almost linear pressure isotherms. Silica-gel satisfies criteria (1) – (5) above, but may pose problems of high cost and availability in most developing countries, like Nigeria (Iloeje, Ndili, 1995, P. 1145).

3. Principle of adsorption
Adsorption occurs at the surface interface of two phases, in which cohesive forces including electrostatic forces and hydrogen bonding, act between the molecules of all substances irrespective of their state of aggregation. Unbalanced surface forces at the phase boundary cause changes in the concentration of molecules at the solid/fluid interact. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate (Khatab, 2002).

Adsorption process can be classified as either physical or chemical, depending on the forces causing the adsorption process. Physical adsorption (physisorption) occurs when Van der Waals forces bind the adsorbing molecules to the solid phase, these Intermolecular forces are as same as ones that bond molecules to the surface of a liquid. Molecules that are physically adsorbed to a solid can be released by applying heat; therefore, the process is reversible. Chemical adsorption (chemisorptions) occurs when covalent or ionic bonds are formed between the adsorbing molecules and the solid substance. The bonding forces of chemical adsorption are much greater than that of physical adsorption. Thus, more heat is liberated. This bonding leads to change in the chemical form of the adsorbed compounds and hence, it is irreversible. For this particular reason, most of the adsorption process applicable to the thermal system or cooling machine mainly involve physical adsorption. It is the general phenomenon resulting from the interaction between a solid (adsorbent) and a gas (refrigerant), based on a physical or chemical reaction process. An adsorption refrigeration machine utilizes the phenomenon of physical adsorption between the refrigerant and a solid adsorbent; the molecules of the refrigerant come to be fixed at the surface of
The adsorbent via connections of the type Van der Waals. It is generally consisted of a generator, a condenser, a pressure-relief valve and an evaporator. The generator consists of a solar plate containing the adsorbent, which is heated by the solar radiation, for desorption of refrigerants. A structure example of this kind of system is illustrated in Fig. 3.1(Khattab, 2004). When fixed adsorbent beds are employed, which is the common practice, these cycles can be operated without any moving parts. On the one hand, the use of fixed beds results in silence, mechanical simplicity, high reliability and a very long lifetime, on the other hand, it also leads to intermittent cycle operation, with adsorbent beds changing between adsorption and desorption stages, which decreases the COP of the system. Hence, when constant flow of vapor from the evaporator is required in order to provide continuous cooling, two or more adsorbent beds must be operated out of phase.

Luo et al (Li,Wang,2002,P.1446) summarized and compared 15 adsorbents (12 activated carbon, 3 zeolite), 4 adsorbates (methanol, ethanol, ammonia, water) under the same conditions, with cycle COP as the same criterion. The results show that methanol/activated carbon PICASOLV is the best among all the studied working pairs. A cycle COP of 0.55 could be achieved at evaporation and condensation temperatures of -5 and 30°C, respectively. Recently, Anyanwu and Ogueke compared (Li,Enibe, 2007) thermodynamically the different systems using activated carbon/methanol, activated carbon/ammonia and zeolite/water adsorbent/adsorbate pairs. It was concluded that zeolite/water is the best pair for air conditioning application while activated carbon/ammonia is preferred for ice making, refrigeration and food preservation. The maximum possible net solar COP was found to be 0.3, 0.19 and 0.16 for zeolite/water, activated carbon/ammonia and activated carbon/methanol, respectively, when a conventional flat plate solar collector was used. But from a practical standpoint, none of these working pairs are perfect. The principal limitation of these cycles lies in the weak mass and heat transfer characteristics of the adsorbent beds. The adsorbents, like the activated carbon, the zeolites or the silica-gel have low thermal conductivities and poor porosity characteristics. The effect is the bulky collector/generator/adsorber component and, thus, its excessive heating capacity, leading to rather low thermal COP. The above difficulty is a real challenge faced by researchers and much effort has been devoted to overcome this inconvenience.
Munyebvu produced activated carbon from monolithic discs housed in a tube with internal fins to improve both its thermal conductivity and thermal contact with metal elements. Li and Wang practically analyzed both parametric effects of collector and environmental parametric effects on performances of solar-powered adsorption refrigerator. The author concluded that the heat transfer and thermal conductivity of the adsorbent beds could be enhanced by adding packing density of adsorbent, adopting double glass covers, using selective coating material as well as using heat transfer fins. Moreover, choosing a suitable environmental condition may improve the performance of solar refrigerator.

![Fig. 3.1. Schematic drawing of a solar adsorption refrigerator (Khattab, 2004)](image-url)
3.2. The Adsorption Cycle

The solar adsorptive cycle is the succession of two periods, the first period consists of regeneration of the adsorbent by solar energy when the adsorbate is condensed and the second period occurs during the night when the evaporation of the adsorbate and the adsorption take place. Adsorption cycles are only intermittent in operation, since the adsorbent cannot move through the components, and the cycle comprises two phases: heating–desorption–condensation phase and cooling–adsorption–evaporation phase. When the thermal energy supply is solar energy, the phases correspond to the natural diurnal and nocturnal solar radiation periods, respectively. In this case, the demand for energy is in phase with its supply. Adsorption cycles have been considered for use in heat pump systems, just as many different absorption cycles. Solar powered adsorption refrigeration contains only three major components (container of adsorbents, condenser and evaporator) and functions as follows. The adsorbent is packed in a sealed container painted black for solar radiation absorption. During the day, solar energy heats the high concentration of adsorbent and container to the maximum cycle temperature (Luo, Dye, 2005, P.666). At its condensing pressure corresponding to a particular temperature, the refrigerant starts desorbing from the adsorbent. As the refrigerant vapor is changed to liquid in the condenser, heat is dissipated to the surroundings. The condensate flows by gravity into a liquid receiver or directly into the evaporator. During the night cycle, the adsorbent is cooled to near ambient temperature, thus reducing the pressure of the entire system. When the adsorbent pressure equals the saturated vapor pressure of the refrigerant, the refrigerant boils in the evaporator and causes heat to be absorbed from the immediate environment. The resulting refrigerant vapor is re-adsorbed into the adsorbent, while cooling is produced. The pressure–temperature–concentration (P–T–X) diagram of Fig.3.2 (Luo, Wang, 2007, P.610-611) illustrates the above processes and their typical operating temperatures. Practically realized solar energy powered solid adsorption refrigeration cycles based on the above principles may be classified according to the adsorbent/refrigerant combination used.
3.3. Intermittent Adsorption Systems for Ice Making

Because of the intermittent nature of the solar energy, intermittent adsorption refrigeration cycles will be considered as logical approaches to solar cooling systems. In this work, just four intermittent systems will be discussed, with their working principles; which is the focus under the adsorption technology for ice making (Nahttab, 2004).

3.4.1. Silica gel – water system.

Since early 1980s, the work on silica gel – water systems have been popular and lot of work was carried out mainly in Japan. In an effort to utilize solar heat, Sadoka and Suzuki (Resstucia, Freni, 2004, P.286) achieved a solar COP of about 0.2 with a solar collector 500X500X500 mm³ depth, packed with 1kg of silica gel particles and with 1.5kg of distilled water in the evaporator. On a clear day with total solar insolation of 19.3 MJ m⁻² per day, it was estimated that a COP of about 0.4 is possible with 0.4m² solar collector.

A solar powered refrigeration system with a 0.25m² flat plate collector has been developed by Boubakri. This system would realize an evaporating temperature of 5°C when the condensation temperature was around 35°C and the
attained regeneration temperature was 100°C. Ortel and Fischer used methanol with silica gel instead of water, so that, the system could operate at an evaporating temperature below 0°C. It was found that a two-chamber silica gel–water system could be operated by methanol also, but because of methanol’s inferior thermodynamic properties, the COP of the system was considerably reduced by about 30%.

3.4.2 Zeolite – water system.

Tchernev (Restuccia, Freni, 2004, P.292) observed that a naturally occurring mineral, called zeolite, adsorbs large amounts of water vapor when cooled and desorbs the water vapor when heated, thus providing a unique opportunity for its utilization in refrigeration applications. Natural zeolite, placed in a hermetically sealed metal container, performs the functions of energy collection and those of mechanical compressor in the conventional refrigerator but without any moving parts. Fig. 3.3 (Restuccia, Freni, 2004) shows that the quantity of water adsorbed by zeolite is strongly dependent on temperature and only weakly dependent on vapor pressure. Therefore, during the refrigeration process at night, when the collector containing zeolite is near ambient temperature, the water is readily adsorbed, keeping the pressure below 0.055 kPa and making the evaporator water freeze. During the day, the regeneration process is only slightly affected by the condensation pressure. Using this principle, Tchernev fabricated and tested a 100 dm³ zeolite–water solar energy powered refrigerator. The collector/generator/absorber component contained 5 cm thick, 50 kg zeolite m⁻². For a solar energy input of 6kW h, the refrigerator produced 900 Wh of cooling per square meter of collector area with a coefficient of performance (COP) of 0.15. Fig. 3.4 (Sumathy, 1999, P.707) shows a schematic diagram of Tchernev’s refrigerator. Successful field testing of this unit sparked interests’ world wide in solar powered solid adsorption refrigeration. However, natural zeolites are difficult to obtain in sufficient quantities in many countries. Consequently synthetic zeolite, particularly molecular sieve 13X, which are easily manufactured, are commonly used.

Dupont et al. investigated two solar powered solid adsorption refrigerators: one utilizing a water cooled condenser, while the other used an air cooled condenser. The working pair for both is zeolite 13X–water. Test results showed that in the water cooled condenser model, the solar COP varied over the range 0.04–0.14 with ice production in the range 3.71 – 8.14 m² of collector area. For the air cooled condenser refrigerator, the solar COP of 0.10 was achieved with 7.0
kg/m² of ice produced. Grenier et al built a large cold store of volume 12 m³ powered by solar energy using a zeolite 13X–water combination. The adsorbent granules were distributed in 24 flat plate type collectors, each of area 0.83 m². The evaporator temperature achieved was as low as 2.5°C, corresponding to a solar COP of 0.086. Comparing these results with those above, reveals that the technology does not show any size advantages and, therefore, could be adaptable to large, small and medium size refrigerators. Phillip et al also built a flat plate solar collector operated, intermittent zeolite 13X–water refrigerator. Their system comprised a box type solar collector of surface area 0.25² containing about 5 kg of adsorbents, tube-in-stagnant water condenser of 0.4 m² heat transfer area, a two litre evaporator constructed from brass and diaphragm valves for isolating the components. Field tests in actual day and night conditions of India indicated that about 3% desorption was obtained, and the maximum cycle temperature was 130°C. Evaporator temperatures as low as 8°C could be attained with 1 kg of ice produced during the night cycle. Apart from zeolite, another adsorbent which adsorbs water is silica–gel which is the combination discussed in the section above.

Fig. 3.3 Adsorption Isotherms of water vapour on zeolite – 13 X(Restuccia,Freni,2004)
3.4.3 **Activated carbon – methanol System**

The most detailed design of a practical solid adsorption refrigerator so far reported in the literature is that of Pons and Guillemino (Sumathy, Zhongfu, 1999, P. 705) that used an activated carbon–methanol combination. This system consisted of four solar collectors of total exposed area 6 m², containing a total of 130 kg of adsorbent, two air cooled condensers and an evaporator with a net production of 30–35 kg of ice per sunny day. Analysis of the experimental data on this ice maker showed the performance to be in the range 0-10 and 0-12 (COP) when the incident solar energy lies between 16 and 19 MJ/m². They concluded that this performance could be improved by reducing the sensible heat of the evaporator, improving the cooling of the collectors and making all their collectors identical. Exell et al. designed and fabricated a charcoal–methanol solar refrigerator with the reactor consisting of an array of 15 copper tubes 54 mm in diameter and 1.2 m long with effective collecting area of about 1 m². The reactor tubes contained 17.8 kg of activated charcoal 207E3, manufactured by Sutcliffe Speak-man Carbons Ltd., United Kingdom. The condenser was water cooled with a heat transfer area of 0.35 m², and the liquid
receiver and evaporator were designed as a single unit housed in a lagged box. Test results showed that the efficiency of the reactor varied between 33% and 44%, and a peak temperature of 122°C was attained during clear days. The net solar COP obtained was above 0.10 and sometimes reached 0.123. The maximum evaporator temperature during most nights was below 7°C, but during some nights it was as low as -12°C. The refrigerator was able to produce up to 4 kg ice per 8\textsuperscript{on} on a clear day. Fig. 3.5 (Sumathy, Zhongfu, 1999) shows the diagram of this unit.

3.4.4 Activated Carbon – Ammonia System

Investigations in the use of charcoal – ammonia are apparently more recent, mainly during the 1990s. Jones (Restuccia, Freni, 2004, P.285) used a novel carbon – molding technique and incorporated a thermal wave regeneration concept employed in the drying of a gas streams; a small unit consuming 0.51 kg of charcoal produced 293W cooling with an adsorbent heating and cooling cycle of 6mins, with ammonia as the adsorbate. With R22 and R134a as adsorbates, cooling rates of 113 and 99 W were reported. Jones (Restuccia, Freni, 2005) also reported that larger multi – bed systems were under development which could have a cooling COP of 1.0.

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Fig 3.5 Schematic diagram of the new solar refrigerator model, developed at AIT by Exell, using Activated carbon – methanol pair. (Sumathy, Zhongfu, 1999, P.705)
In furtherance of the efforts to develop a high pressure adsorbent–refrigerant solar energy operated refrigerator, Critoph (Wang, Way, 2008) also built a laboratory scale activated carbon–ammonia refrigerator. The generator, of exposed surface area 1.4 m², consisted of an array of 15 stainless steel tubes, each of 2 m length, 42 mm outside diameter and 1.1 mm thick, rated to 30 bar pressure. About 17 kg of activated carbon granules were packed in the tubes. The condenser was a 4 m length of 12.5 mm diameter stainless steel tube coiled within a 100 litre water tank. The evaporator was a 10 mm diameter stainless steel coil immersed in 4 litres of water. The evaporator temperature attained was up to -1°C and about 3 kg of ice was produced. The peak collector temperature for the simulated day tests was 115°C, and the solar COP was 0.04. However, the difficulties and practical disadvantages of activated carbon–ammonia systems are the high pressure requirement, resulting in the bulkiness of the refrigerator, and the corrosive nature of the refrigerant, ammonia. The problem of great bulk in large systems can be avoided by the development of rapid cycling units, as have been done. In this version, two separate adsorption cycles are operated out of phase such that when one adsorber is being heated by the energy source, the other cools to ambient temperature, re-adsorbing its refrigerant and producing useful cooling in the evaporator. The laboratory prototype rapid cycling ice maker consisted of two adsorbers: each consisting of seven 2 m long stainless steel tubes, with 1.04 kg of activated carbon in each tube, packed in a hexagonal cell and mixed together. Each hexagonal cell was contained in an outer copper shell of 150 mm diameter that contained steam at 2 bar pressure during the heating phase. Each individual tube had a smaller diameter concentric tube that carried cooling water during the cool down mode. The condenser was water cooled and the evaporator consisted of a simple stainless steel coil soldered around a copper box containing up to 5 litres of water. The results of experiments conducted with this unit showed that the half cycle times for optimum ice production varied from 16min with steam at 150°C to 26min with steam at 100°C.

4. Recent developments in solar technologies

The ever-increasing shortage of fossil fuels, rising gasoline prices, and global warming are causing people and governments to look with greater interest at renewable resources as a viable and more “earth-friendly” option to the energy problem (Xu, Xang, 2007, P375-376). These renewable resources include wind, solar, geothermal and hydrogen power. Within forty minutes of the sun shining on the earth, the sun will have given off as much energy as the entire world
population will use in a year. Only about one percent of this energy put out by the sun is harnessed and utilized by Earth’s inhabitants. The use of solar energy as a power source is not a new one. But the panels developed in the 1970s by Bulat (Xulat, 2007, P.478) were so bulky and large; that very few people could afford them, much less use them. Using technology developed for the computer industry, cells used in Photovoltaic solar collection systems are now thinner and more diversified. Perhaps the greatest advancement in Photovoltaic research has been thin cell solar research, or nanotechnology. This is the use of very tiny cells created through silicon and other minerals to collect solar energy. The creation of nano particles has allowed developers to create shingles coated in these cells as well as to develop a spray-on coating that can be sprayed onto another material, such as the roof of a building. This spray-on coating contains the nano particles and enables other items to also collect solar energy and convert it into electricity. The use of thin cells makes the solar panels smaller and more available to the common consumer. This is because many houses within cities have to conform to specific city codes and may also have to conform to Home Owner Association rules. These rules may not allow the use of solar panels because they are large, visually unappealing, and may obstruct a neighbor’s view. By using thin cells, there will be fewer complaints from the neighbors and if the homeowner uses solar panels that are part of the roofing material, the neighbors won’t see the panels at all. Solar energy can be used not only for generating electricity, but also for heating and even cooling spaces, as well as heating water. Using solar energy for heating and cooling is called Solar Thermal. These systems can be active or passive. If the system is active, then moving parts are involved and if it is passive, than there are no moving parts used in addition to the collection unit. Part of using solar energy for heating and cooling isn’t really using new technology at all. It is more in architectural design and the orientation of the building on the property. Orienting a house so that it can take full advantage of the most sunlight during the day, at any given time of year, as well as ensuring that the longest horizontal lines of the house are facing south are key elements to the design and layout of the building. This is because the south side will get the most sunlight at any time during the year. Also choose building materials that will absorb heat during the day and let it off slowly at night when it is cooler. Heating water can be done with either an active or passive solar thermal system. Passive systems are considered to be the most reliable and most cost effective of the solar thermal systems because there are no moving parts that can break down or will
eventually need replacing. The best part of a passive system is that it is virtually maintenance free. Many small things are solar powered. Some things have been used for awhile now – such as solar powered calculators. Today it is commonplace to find solar panels attached to emergency telephones along many major highways and to find traffic lights and school zone lights also attached to these systems. Solar Power systems are still expensive, but as technology improves and demand for renewable energy sources increases, solar power will become closer to the average person’s grasp (Zano, Margett, 1998, p.32-37). As computer technology progresses and governments supply more funding, companies and universities will spend more time improving this infinite resource. There are many ways that solar energy can be used, from simple cardboard box ovens to self-sufficient homes that rely only on the power of the sun to keep the inhabitants comfortable.

5. SUMMARY AND CONCLUSION
In this work, the review on several research works done by different people has been presented. It also contains the categorization of different adsorbate/adsorbent pairs; stating some specific requirements in the choice of the various pairs. Theoretical adsorption equilibrium models have also been outlined. These are related equations governing the solar adsorption technologies focused on in this work. They enhance the understanding of the physics of the adsorption process applicable to refrigeration. The empirical equations of D – R or D – A, which separate adsorbate and adsorbent properties are generally preferred. Also, adsorption cycle is presented; which is the succession of two periods. The first period consisting of regeneration of the adsorbent by solar energy, when the adsorbate is condensed, and the second periods occurs during the night when the evaporation of the adsorbate and the adsorption takes place. The cycles are only intermittent in operation, since the adsorbent cannot move through the components, and the cycle comprises two cycles. Adsorption cycles have been considered for use in heat pump systems, just as many different absorption cycles. The working principles of four intermittent adsorption systems are reviewed; which are silica gel – water system, zeolite – water system, activated carbon – methanol system and activated carbon – ammonia system. The unique advantages of using an environmentally friendly refrigerant, chemically stable working pair and inexpensive construction materials locally available in developing countries, like Nigeria make solid adsorption solar refrigeration attractive for further
developments, but however, a lot of research works still needs to be done for enhancing the heat and mass transfer to improve performances of solar sorption refrigeration systems. More modern solar energy collecting and transferring technologies, and more advanced optimization and models are also being anticipated. In addition, combined systems and domestic equipments using advanced micro– exchangers are also the trend of development.

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