



Solar systems integrated with absorption heat pumps and thermal energy storages: state of art



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ABSTRACT

Renewable energy sources (including hydropower, wind, biomass, geothermal, tidal, wave and solar energy sources) can satisfy the present and future energy demands, with minor environmental impact respect to traditional sources of energy. Solar energy is the cheapest and widely available renewable energy and solar cooling systems are a green cold production technology that produce minor CO₂ emissions due to use of heat pumps. In fact, absorption refrigeration is a mature technology that has proved its applicability with the possibility to be driven by low grade solar energy. In this context, thermal storage systems contribute to balance the disadvantages of the intermittent nature of solar energy and the variation in cooling demand, receiving more attention of researchers in the recent years.

This paper presents an innovative and comprehensive literature review on solar systems integrated with environmental-friendly processes as absorption heat pumps and thermal energy storages. A study about processes regarding the renewable and sustainable energy according the European policy is carried out.

Photovoltaic and photovoltaic/thermal solar systems can be used to this purpose and are the most promising technologies growing very fast in recent years.

Researches show that one, half, two effect of absorption heat pumps integrated with solar systems and thermal energy storages can be an attractive alternative in cooling systems, meeting the demands for energy conservation and environmental protection. Showing various systems, a discussion about the improvement of cooling applications respecting the environment is also presented in this paper.

1. Introduction

Energy has an important role in all kind of activities: the growing demand for energy resources, the escalating fossil fuel prices and global warming have improved the sustainable energy resources reducing the impact on the environment.

The European Commission Regulation 2037/2000, activated on 1 October 2000, aims to control and program all the ozone depleting materials so all HCFCs (hydro-chlorofluorocarbons) will be forbidden by 2015 [1]. The goal is to find an alternative to fossil fuels before they deplete and/or destroy the earth: the energy required by the world is estimated to increase by 50% from 2005 to 2030 due to the population growth and economic development.

The European strategy to decrease the energy dependence follows two principles: the diversification of energy sources and the policies to control the consumptions. The key to diversification is the use of renewable energy sources (RES), according the sustainable development [2]. The term “renewable energy”, as hydropower, wind, biomass, geothermal, tidal, wave and solar energy sources, means that the

energy is produced from a natural resource with the characteristics of inexhaustibility and natural renewability over time. Renewable energy sources can satisfy present and future energy demands without environmental impacts. However, RES resources, except biomass, geothermal and hydro, have an intermittent nature, so it is necessary an energy storage system to use them in an effectively way [3,4]. Due to the high investment costs in the storage systems, the usage of renewable energy sources is becoming more expensive [5,6]. The common goal of the European Union (EU) is to increase the share of RES in the final energy consumption to 20% in 2020 and to reduce GHG emissions by 20% until 2020 in comparison to their levels in 1990, and by 30% until 2030 if the other developed countries undertake similar steps.

This alternative is the best option that will increase the variety in energy resources and may solve several problems as: the replacement of fossil resources, the decrease of foreign dependency in fossil fuel and the elimination of air pollutions caused by hazardous gases.

Among all environmentally friendly and naturally available sources, solar energy is the main renewable energy sources, being a clean and sustainable resources.

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In order to have a rational use of energy resources, solar energy can play an important role [7] and can provide cheap and clean energy for cooling and refrigeration applications, all over the world. The renewable energy technologies supply approximately the 13.3% of the world's energy demands [8].

The development of solar refrigeration technologies is a worldwide focal point.

To this purpose a combination of solar energy and heat pump shows potential for different industrial applications [9].

Cooling can be achieved through two basic methods. The first is a photovoltaic system (PV), where solar energy is converted into electrical energy and is used for refrigeration much like conventional methods [10]. The second one utilizes a solar thermal refrigeration system (PV/T), where a solar collector directly heats the refrigerant through collector tubes [11]. However, the solar energy is intermittent so thermal storage system is critical: it ensure a more renewable energy use and energy efficiency respect to conventional systems. Also energy storage has an increasing attention in many industrial and commercial applications and it is one of the most appropriate methods of correcting the mismatch that occurs between the supply and demand of energy. Heat can be stored in different way as in sensible, latent and thermochemical form. In sensible heat storage, thermal energy is stored by raising the temperature of a solid or liquid. In the latent heat storage, a phase change material (PCM) has a phase change, absorbing and releasing heat. In thermo-chemical heat storage systems, the heat is stored whit an endothermic chemical reaction.

Solar cooling technology is still in an early stage of development as shown in several research works. Problems for this system are the associated costs and the energy efficiency. For this reasons new design options with regard to solar collectors, auxiliary energy system and cooling modes are evaluated. It is shown that solar cooling systems would not be competitive compared with standard cooling systems at present energy prices. Beside the high cost, the main obstacles for large application of solar cooling system are the lack of practical experience in design, control and operation of these system. In this article an innovative review about the solar cooling technology with environmental aspect, according the European legislation, is presented.

The purpose of this research is to review the studies of solar systems and their integration with absorption heat pumps and thermal energy storages in order to produce cold: absorption heat pumps and thermal energy storages have a key role in the environmental sustainability and energy efficiency.

Infect, the use of renewable energy and the recovery of waste energy are unique strengths of the absorption heat pumps because they can be directly driven by low-grade heat sources as solar energy, geothermal energy, biomass energy and waste energy [12]. While thermal energy storage has an important role in matching energy supply with energy demand, which is especially significant in low-grade energy uses, such as solar energy and waste heat.

In the literature there are only the work of Kamel and Fung [13] about the review of conventional compression heat pumps integrated with solar systems in technologies called solar assisted heat pumps (SAHPs) and the work of Hassan and Mohamad [14–17] regarding a review about absorption heat pumps integrated in solar systems.

Literature studies regarding the integration of solar systems with thermal energy storages and absorption heat pumps are not present. In this way a solar system is studied with some integrated and the more environmental friendly processes in order to produce cold. These systems have low ozone depletion and limited global warming potential. Also, suggestions about the design of solar cooling systems are given in this paper.

2. Solar refrigeration systems

2.1. Solar photovoltaic systems

Photovoltaic systems allow the direct conversion of radiations into electricity through a photoelectric effect, infect the term “photo” means light while “voltaic” electricity. To this purpose, photovoltaic systems have cells able to convert sun-light into electricity. Cells have layers of a semi-conducting material, so the light creates an electric field across the layers, that produces electricity. The intensity of the light determines the electrical power generated by each cell. Researches on semiconductors (III–V and II–VI), based on solar cells, were studied since 1960 and at that time, new technologies for polycrystalline Si and thin-film solar cells have been establish to have lower material costs and energy input, but a higher production capacity. The efficiency of the photovoltaic modules is influenced by several parameters as solar irradiance, packing factor, and cell temperature. With high solar irradiance a large number of electrons is released, determining a more electrical current. Increasing the packing factor (the fraction of absorber plate area covered by the solar cells) results in more current per unit collector area. However, these two parameters increase the cell temperature, decreasing the efficiency of the module: PV efficiency decreases as PV module temperature increases, because high PV cell temperature reduce the voltage significantly. The commercial PV modules, in general, have an efficiency in a range of 6–16% at temperature of 298 K [18]. This relatively low efficiency is much smaller compared to thermal efficiency. The production of electricity causes the generation of heat, which has a great influence on the dropping performance of electrical yield. Study carried out by Othman et al. [19] reports that for every 274 K increase in PV panel, there is about 0.4–0.5% decrement in its efficiency.

For this reason, it is necessary to cool the photovoltaic modules by some means to enhance the efficiency and to convert the waste heat into useful thermal energy for different applications. Fig. 1 shows different assessment of PV systems using air and water as a heat transfer fluid, with and without glazing: (a) PV/water, (b) PV/water + glazing, (c) PV/air, and (d) PV/air + glazing.

Results show that water allows to remove heat with a more efficiency compared to air, increasing the electrical efficiency. Using glazing provide up to a 30% increase in thermal efficiency compared to basic systems, due to the suppression of thermal losses.

In general, PV cells produce direct current (DC) electricity, but most domestic and industrial electrical appliances produce alternating current (AC). Therefore, a complete PV cooling system typically have these components: photovoltaic modules, a battery, an inverter circuit and a vapor compression AC unit. The PV modules produce electricity by converting light energy (from the sun) into direct current (DC) electrical energy. The battery is used for storing DC voltages at a charging mode when sun light is available and supplying DC electrical energy in a discharging mode in the absence of day light. A battery charge regulator can be used to protect the battery from overcharging. The inverter is an electrical circuit that converts the DC electrical power into AC and then delivers the electrical energy to the AC loads. The vapor compression AC unit is actually a conventional cooling or refrigeration system that is run by the power received from the inverter. Fig. 2 shows different configurations of PV systems: standalone system, a hybrid system (working with an oil/hydro/gas/wind power plant) or as a grid system respectively in Fig. 2a, b, c. The grid system is the simplest scheme, while a hybrid system allows to use other renewable energy.

The efficiency of PV modules can be increased by using inverters, but the COP and efficiency are still not desirable.

2.2. Solar photovoltaic/thermal systems

The solar photovoltaic/thermal systems born in the 1970 s and respect to PV cooling systems can utilize more incident sunlight. The

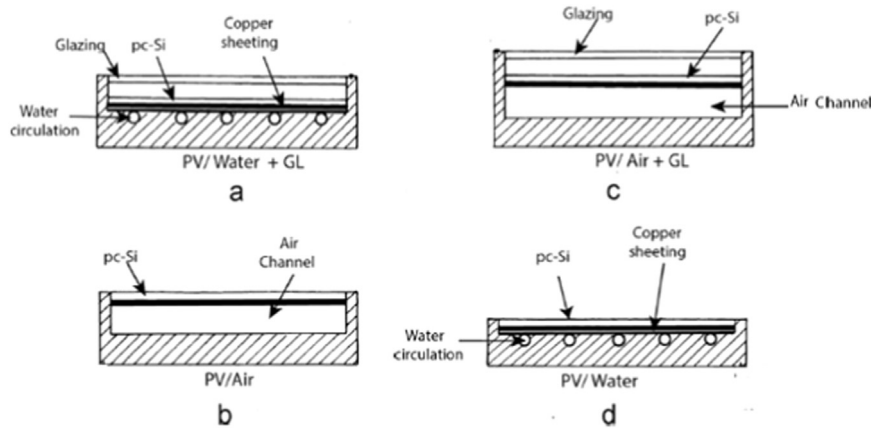


Fig. 1. Cross section of PV models: a) PV/water+glazing, b) PV/air c) PV/air+glazing (d) PV/water.

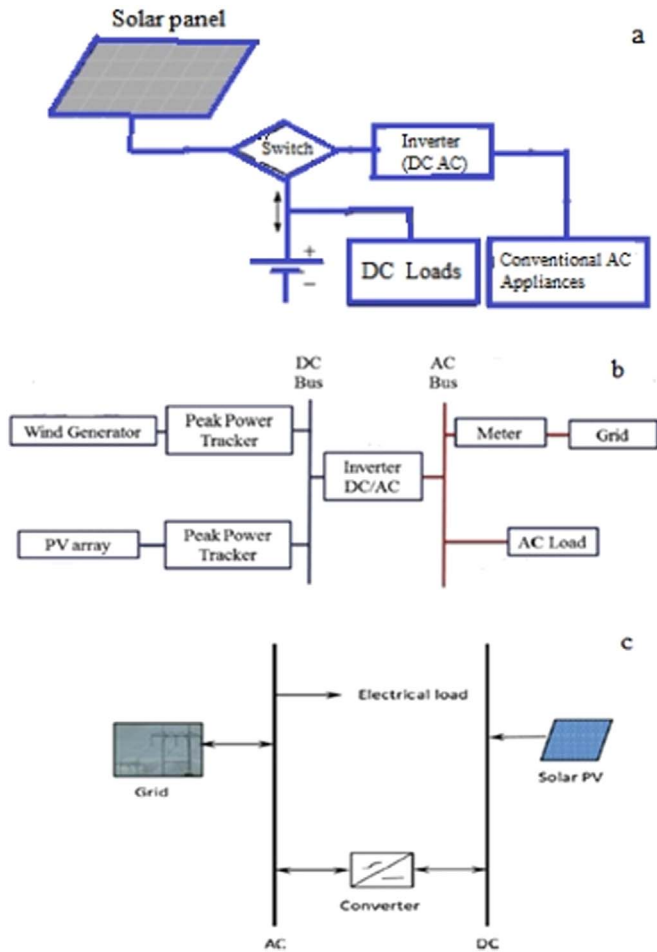


Fig. 2. a) Schematic of a stand-alone PV system; b) Schematic of a hybrid PV-wind energy system configuration; c) Schematic diagram of the solar PV and grid-connected system.

system produces electricity and also acts as a thermal absorber. A solar collector is linked with a photovoltaic panel to extract the excess heat from the module and to reduce the cell temperature, improving the cell efficiency. A fluid, in general, air, water, glycol, oil is used as a heat transfer medium in the solar collector. The thermal energy produced by solar collector can be used in space heating, water heating, and steam generation or stored in thermal storage. The solar thermal collector is classified according to the fluid type: liquid heating and air heating, with different channel shapes and flow patterns. Air and liquid can be used in the same collector. The working fluid is chosen carefully,

considering the solar radiation in the local area, the heat capacity of the fluid, the design configuration, and the range of temperature. A PV/T collector, shown schematically in Fig. 3, typically consists of a PV module on the back of which an absorber plate is attached.

Fig. 3a shows a cross section of a PV/T collector: the module is composed of several “layers” made of different materials, such as glass, silicon (solar cell), EVA, copper (flow channel), fluids, and insulating materials that function as a hybrid electrical/thermal collector; Fig. 3b shows the main dimensions of these systems.

Zondag et al. [20] differentiates four main types of PV/T system, according to the water flow pattern and the heat exchange method: sheet and tube, channel, free-flow and two-absorber types. Considering the type of energy collection, solar collectors can be classified as flat plates, evacuated tubes and concentrating collectors [21], glazed or unglazed as covered panels [8]. In glazed type, a cover of the glass is placed over the absorber in order to reduce the thermal losses. Glazed collectors produce higher thermal energy, used in medium and high temperature applications, but can be damaged due to the hot spots, reducing electrical yield. Flat-plate solar collectors are the most used systems, with a metallic absorber and an insulated casing topped with glass plates. Evacuated collectors have less heat losses and better efficiency at high temperatures and they are typically realized in a glass tube inside in an evacuated glass tube, to withstand the pressure difference between the vacuum and the atmosphere. The thermal efficiency and electrical efficiency of a PV/T collector are, respectively, given by (see Eqs. (1) and (2)):

$$\eta_t = \frac{m \cdot C \cdot (T_{out} - T)}{G \cdot A} \quad (1)$$

$$\eta_e = \frac{V_{mpp} \cdot I_{mpp}}{G \cdot A} \quad (2)$$

where m and C are, respectively, the mass flow rate and specific heat capacity of the coolant, A the collector aperture area, T_{in} and T_{out} the coolant temperatures at the inlet and outlet respectively, G the incident solar irradiance normal to surface, V_{mpp} and I_{mpp} are the voltage and electric current at maximum power point operation respectively. The electrical efficiency is provided by (see Eq. (3)):

$$\eta_e = \frac{A_{cell} \cdot \eta_{cell}}{A} \quad (3)$$

where η_{cell} is the cell efficiency, A_{cell} the cell surface area, A the aperture area. The energy saving efficiency is then provided as in the work of Chow et al. [22] (see Eq. (4)):

$$\eta_{saving} = \frac{\eta_e}{\eta_{power}} + \eta_t \quad (4)$$

where η_{power} is the electric power generation efficiency of conventional power plant. The total conversion efficiency of solar energy into

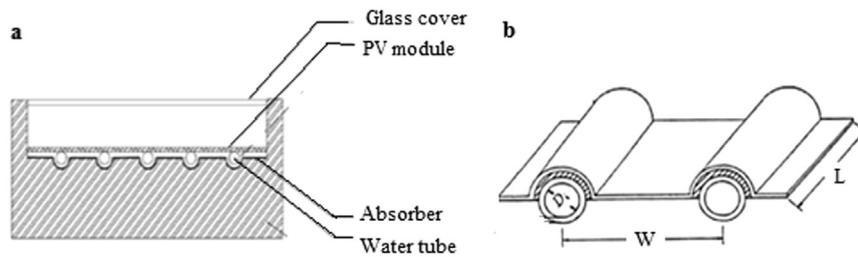


Fig. 3. a) Cross section of a PV/T collector, b) Schematic of an absorber plate showing the various dimensions.

electricity and heat is the main parameter that characterizes the performance of PV/T collector. In many researches, it is simply defined as the total amount of thermal and electrical efficiency, according to (see the Eq. (5)) [23–30]:

$$\eta_{tot} = \eta_{th} + \eta_{el} \quad (5)$$

Several researches and development works on PV/T systems are carried out in the last 35 years with a gradual increase in the level of activities. Nevertheless, real project applications are still limited.

3. Absorption heat pumps integrated in solar refrigeration systems

Absorption heat pumps, in general, are used for solar refrigerations: they require very low or no electric input and, for the same capacity, the dimensions are smaller than an adsorption system due to the high heat transfer coefficient of the absorbent. These systems require low thermal energy source and have few moving parts producing low noise and vibration levels. Absorption systems operating in heat pumps mode have become competitive with the most widely used vapor compression heat pumps, in terms of environmental impact as well as energy efficiency; they have further advantages of operating with environmentally clean working fluids and to have a lower electricity consumption, so CO₂ emissions are very low. In addition, absorption heat pumps can be used for large-scale applications and their cost is lower respect to other thermally-driven systems.

Cold production through absorption cycles is the most desirable application in solar cooling technologies [31].

The refrigerant side of the absorption system essentially works with the same principle of vapor compression system [14]. However, the mechanical compressor used in the vapor compression cycle is replaced by the thermal compressor in the absorption system, that have the absorber, the generator, the solution pump, and the expansion valve. The attraction of the absorption systems is that any types of heat source, including solar heat and waste heat, can be utilized in the desorber. According the thermodynamic cycle, the absorption systems can be divided into three categories: single-, half-, and multi-effect (double-effect and triple-effect) solar absorption cycles. In the single-effect and half effect chillers, lower hot-water temperatures respect to multi-effect systems are required [32]. The multi-effect absorption cycles require high temperatures above 358 K, that can be provided by the evacuated tube or concentrating-type collectors. There are three types of cooling production devices: closed cycle continuous absorption cooling system, closed cycle intermittent absorption cooling system and open cycle absorption cooling system.

3.1. One effect absorption heat pumps integrated in solar refrigeration systems

The operation of these systems starts at the absorber where the refrigerant vapor coming from the refrigerator is absorbed and forms a rich mixture. The absorption process is exothermic so, the latent heat related to vapor liquid transformation is released to the ambient in order to keep the absorber at the evaporator low pressure. The

circulating pump brings the rich solution from the absorber low pressure towards the generator, or the desorber, that is a high-pressure zone. The generator uses the heat of solar collectors to separate the refrigerant fluid from the absorbent fluid. The poor solution goes to the absorber by passing through a pressure-relief valve. The solution heat exchanger is used for internal heat recovery in order to improve the efficiency: the solution leaving the absorber is preheated by the hot concentrated solution leaving the generator. The desorbed refrigerant vapor flows towards the traditional cycle composed of condenser, expansion valve and evaporator. The main components for one effect solar assisted absorption cooling system (solar collector or concentrator, a hot fluid storage tank, an auxiliary heater, condenser, evaporator, and the thermal compressor composed of a generator containing the absorber, and the mixture circulating pump) are shown in the schematic diagram of Fig. 4.

Solar flat plate collectors or an evacuated tubular collectors are in general used.

3.2. Half effect absorption heat pumps integrated in solar refrigeration systems

The half effect cycles provide cold using low driving temperature. A schematic diagram for this cycle is shown in Fig. 5. The COP is roughly half of the single effect cycle.

The half-effect absorption refrigeration system consists of condenser, evaporator, two generators, two absorbers, two pumps, two solution heat exchangers, two solution reducing valves and a refrigerant expansion valve. The system is called half-effect because the vapor generated in the generator is divided into two streams as indicated in figure: one goes in the evaporator generating the cooling effect, and the other flow is directed to the absorber in order to reduce its temperature.

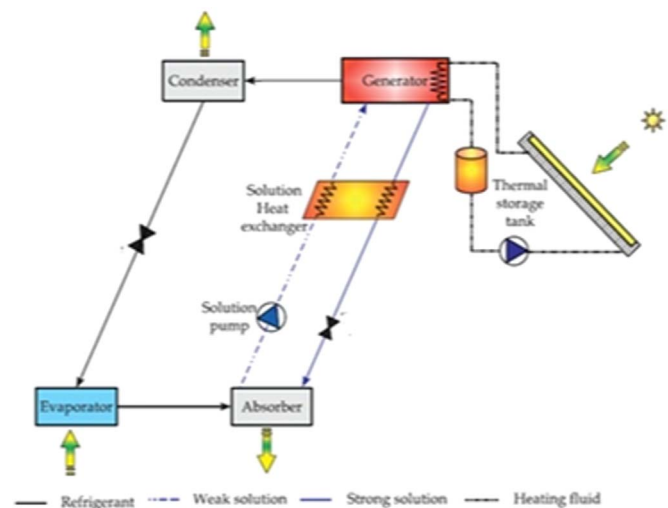


Fig. 4. Schematic diagram for the single effect absorption heat pump in solar cooling system.

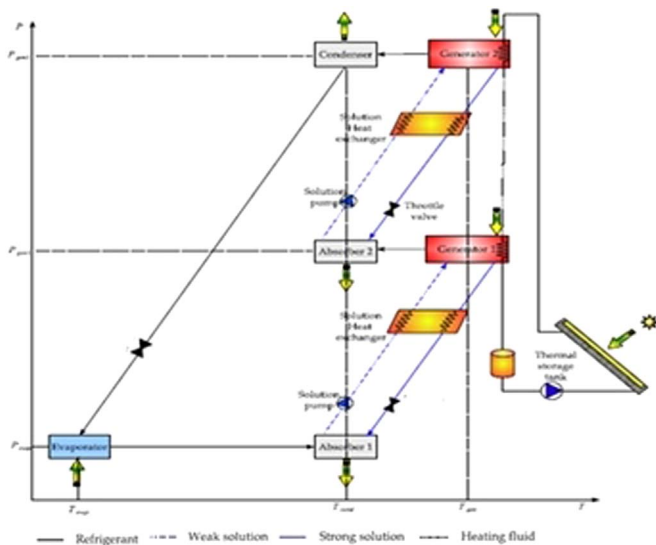


Fig. 5. Schematic diagram for the half effect absorption heat pump in solar cooling system.

3.3. Double effect absorption heat pumps integrated in solar refrigeration systems

Double effect system can be obtained by adding an extra stage as a topping cycle on the single effect cycle: it can provide a more conversion of solar energy and less primary energy use. Double-effect absorption cooling technology was launched in 1956 in order to use a system within a heat source at higher temperatures [33]. These systems have a double COP value compared with that of single effect systems, nearly 1.2. However, their working liquids must achieve higher temperatures, more than 403 K, which is beyond the range for which most solar collectors are designed. As shown in Fig. 6, the high pressure generator is driven by conventional energy and natural gas. The main components are solar collector or concentrator, a hot fluid storage tank, two auxiliary heaters, two condensers, an evaporator, and the thermal compressor composed of two generators containing the absorber, and the mixture circulating pump.

Solar energy, together with the water vapor generated in the high pressure generator, supply energy to the low pressure generator, with a

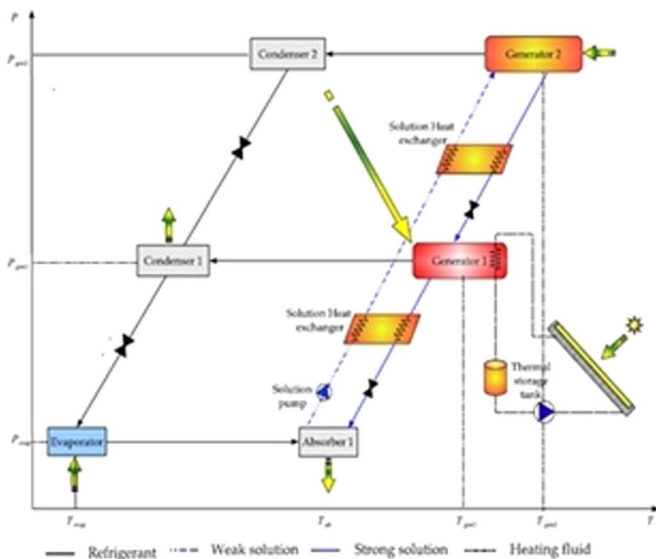


Fig. 6. Schematic diagram for the double effect absorption heat pump in solar cooling system.

temperature closed to 363 K. Many researchers have studied and analyzed the double effect absorption cooling machines [34], but few studies related to the solar driven or solar assisted double effect absorption chillers are found in the literature.

In general, it is necessary to install auxiliary energy systems, as gas fired auxiliary boiler, to supplement the solar-powered cooling systems.

4. Working pairs used in absorption heat pumps

The mainly used refrigerant-absorbent working pairs in the absorption refrigeration systems are H_2O – LiBr , and NH_3 – H_2O pairs. They differ in physical and thermodynamic properties and the choice has a great effect on system performance. The choice depends on different requirements:

1. the refrigerant latent heat should be high, in order to minimize the circulation rate of the refrigerant and absorbent.
2. the refrigerant/absorbent pair should not form a solid phase during the operation.
3. the refrigerant should be much more volatile than the absorbent so the two can be separated without a rectifier.
4. the absorbent should have a strong affinity for the refrigerant, so less absorbent is circulated for the same refrigeration effect, reducing sensible heat losses and liquid heat exchanger.
5. moderate operating pressure is required. Infact high pressure requires heavy-walled equipment, and a higher electrical power is required to pump fluids from the low-pressure side to the high pressure side. While, low pressure requires large-volume equipment that reduces pressure drop in the refrigerant vapor paths.
6. high chemical stability is required to avoid undesirable formation of gases, solids, or corrosive substances.

Different other working fluids have been analyzed for absorption systems. In literature, the review of Macriss et al. [35] provide 40 refrigerant compounds and 200 absorption compounds. Another exhaustive study is the report of IEA Heat Pump Center about some additional mixtures [36]. Nevertheless, the most common working fluids with practical application in absorption systems are H_2O – NH_3 and LiBr – H_2O . Recently, ternary (LiBr , LiNO_3 and LiCl) and quaternary (LiBr , LiI , LiNO_3 and LiCl) salt mixtures have shown promising results: these mixtures are subject of investigation by several authors [37,38]. A summary of the possible working pairs for absorption heat pumps is shown in Table 1: the main used solvent is water with salts, acids and bases in binary or ternary solutions. Water with LiBr based on multicomponent salt mixtures is also used. However, the properties of ternary working fluids require further researches to develop the design and simulation of these absorption systems.

The advantages of $\text{LiBr}/\text{H}_2\text{O}$ are high safety, volatility ratio, affinity, stability and latent heat. Water is the refrigerant, which evaporates at very low pressures producing the cooling effect. Water freezes at below 273 K, so the minimum chilled water temperature in the absorption system with H_2O – LiBr is around 278 K. This is the reason that these systems are used for air-conditioning applications and cannot be used for low temperature refrigeration. These systems operate under high vacuum pressures and the lithium bromide solution is corrosive to some metals, as steel or copper, used for the construction of the system. Corrosion inhibitors may be used for this problem, protecting the metal parts and improving the heat and mass transfer performance. The absorption systems with $\text{NH}_3}/\text{H}_2\text{O}$ operate at moderate pressure and no vacuum is required till 243 K. The advantage of this working pair is that ammonia is completely soluble in water at all concentrations, avoiding risk of crystallization. Also dry coolers can be applied, since the pressure in the system is higher than the atmospheric pressure. Ammonia is both toxic and flammable, and being incompatibility with materials such as copper or brass, steel is normally used. In addition, small temperature difference between the boiling points of the refrig-

Table 1

Summary of working pairs used in absorption heat pumps.

Refrigerant	Absorbent (s)
H ₂ O	Salts
	Alkali halides
	LiBr
	LiClO ₃
	LiBr based multicomponent salt mixtures (LiBr + single salt, LiBr + binary salt system, LiBr + ternary salt system)
	CaCl ₂
	ZnCl ₂
	ZnBr
	Alkali nitrates
	Alkali thiocyanates
	Bases
	Alkali hydroxides
	Acids
	H ₂ SO ₄
	H ₂ PO ₄
NH ₃	H ₂ O
	LiNO ₃
	LiNO ₃ +H ₂ O
	Alkali thiocyanates
TFE (Organic)	NMP
	E181
	DMF
	Pyrrolidone
SO ₂	Organic solvents

erant and the absorbent requires an additional device to obtain a high purity vapor of the refrigerant. This device called rectifier cools the vapor produced in the generator, demanding more supply heat and generating lower COP.

5. State of art about absorption heat pumps with Li-Br/H₂O for solar cooling

The majority of solar cooling systems are based on LiBr/H₂O absorption heat pumps and are driven by hot water from an ordinary flat plate or evacuated tubular solar collector. Table 2 shows works that are present in literature about the absorption heat pumps with H₂O–LiBr pairs.

Absorption heat pumps with one, half, two and three effect are discussed considering the $\eta_{cooling-heating}$, the area of collector and the heat of evaporator. It is evident that the absorption heat pumps with one effect are the most used for space cooling applications. Absorption heat pumps with three and one half effect are few used.

5.1. Half-effect absorption heat pumps with Li-Br/H₂O for solar cooling

The primary feature of the half-effect absorption heat pumps is that they can operate at lower temperature respect to other systems.

Gebreslassie et al. [87] compare various systems in terms of performance and manufacturing cost to investigate the feasibility of low-price air-cooled solar absorption cooling system. They find that half effect systems would require about 40% more heat exchange surface and 10–60% more collector area respect to a single effect system of the same cooling capacity.

Arivazhagan et al. [40] develop an experiment with two stage half-effect absorption system using R134a/DMAC, as working pair: the evaporation temperature is of 266 K while the generator temperature varying from 328 K to 348 K. They conclude that within the optimum temperature range (338–343 K), the value of COP can be about of 0.36.

Sumathy et al. [38] propose two-stage of H₂O/LiBr absorption heat pumps for cooling purposes in South China. Integrating a solar cooling

Table 2State of art about absorption heat pumps with Li-Br/H₂O in solar cooling (a Flat plate collectors, b Evacuated tube collectors, c Trough collectors, d where not given, a collector efficiency of 0,5 has been assumed, e parabolic solar collectors).

References	Application	Q _c [kw]	A _s [m ²]	$\eta_{cooling-heating}$
Half-effect LiBr-H₂O				
[39]	Space cooling			0.36
[40]	Space cooling			0.38
[41]	Space cooling			
[42]				
Single effect LiBr-H₂O				
[43]	Space cooling/ heating			
[44]	Space cooling/ heating			
[45]	Space cooling/ heating			
[46]	Space cooling	4	36a	0.11
[47]	Space cooling	210	1577b	0.31
[48]	Space cooling	90	316a	0.26–0.36
[49]	Air conditioning	4.7	38a	
[50]	Space cooling	11	15	
[51]	Space cooling	10.5		
[52]	Space cooling			
[53]	Space cooling			
[54]	Space cooling	35	49.9a	0.5
[55]	Prototype chiller	10		
[56]	Space cooling	3.5	35b	
[57]	Space cooling	35	50a	0.34
[58]	Prototype chiller	10		0.37
[59]	Prototype chiller			
[60]	Prototype chiller	16		0.4
[61]	Space cooling			0.37
[62]	Space cooling	11	30a	
[63]	LPG-fired solar assisted prototype		72b	
[64]	Space cooling	17.5	57.6	
[65]	Space cooling	35.17	108	0.352–0.492
[66]	Space cooling	35	50	0.35
[67]	Space cooling			
[68]	Space cooling	70	160a	0.6
[69]	Prototype chiller	4.5	12b	0.6
[70]	Space cooling	70	108b	
[71]	Gas heater solar assisted	16	52e	
[72]	Space cooling	70	124a	
[73]	Space cooling	30		
Double effect LiBr-H₂O				
[74]	Fuel fired solar assisted prototype			
[75]	Fuel fired solar assisted prototype			
[76]				
[77]	Space cooling			
[78]	Space cooling	4.7	38a	
[79]				
[80]	Gas heater solar assisted	10		
[81]		5.4–10.7		
[82]	Space cooling	50	230e	
[83]	Cooling/steam generation	140	180c	0.5–0.6
[84]	Space cooling			0.7
[85]				
Triple effect LiBr-H₂O				
[86]	Space cooling			
[87]	Space cooling			

system with these chillers, they obtain a cooling capacity of 100 kW. In addition, the system has a nearly equivalent COP as the conventional cooling system, but at a 50% reduced cost.

Izquierdo et al. [39] design a solar double-stage absorption plant with $\text{H}_2\text{O}/\text{LiBr}$, using flat plate collectors to feed the generator. At condensation temperature of 323 K, the COP is 0.38 while the generation temperature is of 353 K. They also perform an exergetic analysis of this system and find that the single-effect system has 22% more exergetic efficiency than the double-stage half-effect system.

Figueredo et al. [88] study the behavior of a double-stage absorption chiller with 200 kW of cooling power. The modeled system can operate in summer as a double-stage chiller driven by heat at 443 K from natural gas and as a single-stage chiller driven by heat at 363 K from solar energy, or simultaneously. It can also operate during winter in double-stage system for heating purpose, using heat at 443 K from natural gas.

5.2. One-effect absorption heat pumps with $\text{Li-Br}/\text{H}_2\text{O}$ for solar cooling

Nakahara et al. [89] develop a single-effect $\text{H}_2\text{O}/\text{LiBr}$ absorption chiller of 7 kW cooling capacity, with 32.2 m^2 of flat plate solar collectors. The thermal energy produced by solar collector is stored in a 2.5 m^3 of hot-water storage tank. The COP has a value of 0.4–0.8 at the generator temperature of 343–373 K.

Li and Sumathy [85] study a $\text{H}_2\text{O}/\text{LiBr}$ absorption system with a partitioned hot-water storage tank. The system consists of a 38 m^2 flat plate collector and a 4.7 kW absorption chiller: a value of COP (approximately 0.7) of 15% more than a conventional whole-tank mode system is obtained.

Another study on a $\text{H}_2\text{O}/\text{LiBr}$ absorption system with 49.9 m^2 of flat plate collector is developed by Syed et al. [90]. The system performs cooling about 35 kW within generator temperatures of 338–363 K. They calculate three different COPs and an average collector efficiency of approximately 50%.

Chinnappa et al. [91] propose a conventional vapor compression system cascaded with a solar-assisted $\text{H}_2\text{O}/\text{LiBr}$ absorption system. The hybrid system can have a value of COP equal to 5, higher than vapor compression cycle.

Li and Sumathy [48] study experimentally the performance of a solar powered absorption air conditioning system with a partitioned hot water storage tank. They develop a flat-plate collector with a 38 m^2 surface area to drive a single-effect $\text{LiBr-H}_2\text{O}$ absorption chiller of 4.7 kW cooling capacity. The thermal energy produced by solar collector is stored in a 2.75 m^3 hot-water storage tank, which is partitioned into two parts. The upper part has a volume of about one-fourth of the entire tank. Their experimental results during the summer period show that the COP is 0.07, about 15% higher than with traditional whole-tank mode.

Syed et al. [90] report experimental results derived through field testing of a part load solar energized cooling system for typical Spanish houses in Madrid during the summer period of 2003. Twenty flat-plate collector modules with an absorber area of 2.5 m^2 each and a single-effect $\text{LiBr}/\text{H}_2\text{O}$ absorption chiller of 35 kW nominal cooling capacity are used. Pongtornkulpanich et al. [62] develop a solar system with single-effect absorption heat pump that is designed and installed at the School of Renewable Energy Technology in Thailand. The system is sized to satisfy 150% of the calculated maximum cooling load. The authors collect data on the system's operation during 2006 and analyze it to find the extent to which solar energy replaced conventional energy sources. They find that 72 m^2 evacuated tube solar collector supports an average yearly solar fraction of 81%, while the remaining 19% of thermal energy required by the chiller is supplied by a LPG-fired back up heating unit.

Rosiek and Batlles [67] study a solar-assisted air-conditioning system installed in the Solar Energy Research Center (CIESOL)

situated in the Campus of University of Almeria in Spain. This system consists mainly of flat-plate solar collectors with the area of 160 m^2 and a single effect $\text{H}_2\text{O-LiBr}$ absorption chiller with the cooling capacity of 70 kW. Experimental results during one year of operation show that the solar collectors provide sufficient energy to the absorption chiller during the summer mode satisfying the heating demand. The absorption system has an average values of COP about 0.6 and a cooling capacity of 40 kW in summer.

Ortiz et al. [69] show a numerical model of a solar thermal system for a 7000 m^2 of educational building, situated in a high-desert climate. The solar collector array uses both flat plates and vacuum tubes. Results show that the solar cooling system can reduce the total external cooling energy requirement by between 33% and 43%.

Mammoli et al. [71] find that the solar cooling system could supply approximately the 18% of the total cooling load. This percentage could be increased to 36% by tuning the air handler operation and by improving the insulation in the storage tank.

A domestic-scale prototype experimental solar cooling system based on $\text{LiBr}/\text{H}_2\text{O}$ is developed and tested by Aggenim et al. [68] in Cardiff University, UK. The absorption chiller is 4.5 kW and is driven by 12 m^2 vacuum tube solar collector. The system performance is obtained by physical measurements of the daily solar radiation, ambient temperature, inlet and outlet fluid temperatures, mass flow rates and electrical consumption. The average solar coefficient of performance of the system is 0.58 with average peak insulation of $800\text{ W}/\text{m}^2$. In addition to these works, a solar-driven 30 kW $\text{LiBr}/\text{H}_2\text{O}$ single-effect absorption cooling system which has been designed and installed at Institut Universitaire Technologique of Saint Pierre is presented by Praene et al. [72]. The solar collector is composed of 3×3 of series evacuate tubes that produce hot water to move the absorption chiller from 8:00 AM to 5:00 PM. The system allows to have a temperature inside the classrooms of about 298 K.

An experimental and simulation analysis of a laboratory single-stage $\text{H}_2\text{O-LiBr}$ absorption chiller with a cooling capacity of 14 kW is carried out by Bakhtiari et al. [92]. The cooling capacity and COP are measured at different temperatures of chilled, cooling and hot water and, different flow rates of cooling and hot water. Results show that the heat pump can run over a wide range of generator input energy and chilled water temperature; also the cooling water flow rate and temperature significantly affect the performance of the machine. In addition, results suggest that the absorption heat pump has almost a constant COP over a large hot water inlet temperature. Mazloumi et al. [63] simulate a single effect absorption cooling system in Ahwaz, Iran. The solar energy is absorbed by a horizontal N-S parabolic trough collector and stored in a thermal storage tank. The system is designed to provide 17.5 kW of cooling load. A research project with the purpose to evaluate the feasibility of the solar absorption cooling is carried out by Balghouthi et al. [61]. The simulation is developed using TRNSYS and EES programs. They find that the optimized system for a typical building of 150 m^2 is composed by a water lithium bromide absorption chiller with a capacity of 11 kW, by a 30 m^2 of flat plate solar collectors tilted of 35° from the horizontal and by a 0.8 m^3 hot water storage tank.

The performance and cost of a CPVT system with single effect absorption cooling are investigated in by Mittelman et al. [60]. Results show that under a wide range of economic conditions, the combined solar cooling and power generation plant can be comparable to the conventional alternative.

Various cycle configurations with water-lithium bromide solution are simulated by Atmaca and Yigit [50]. Rodriguez et al. [65] develop a system with 50 m^2 of flat-plate solar collectors, that feeds 35 kW of single-effect $\text{LiBr}/\text{H}_2\text{O}$ absorption machine. The chiller works at partial load with a value of COP equal to 0.33.

Florides et al. [49] design a $\text{LiBr}/\text{H}_2\text{O}$ absorption unit with the cooling capacity of 11 kW for a typical model house in Cyprus. The optimum system has 15 m^2 of compound parabolic collectors tilted at 30° from horizontal and a 600 l of hot water storage tank.

Assilzadeh et al. [55] design a solar cooling system for Malaysia and similar tropical region using evacuated tubular solar collectors and a LiBr/H₂O absorption unit. It is shown that a 0.8 m³ of hot water storage tank is needed to have a continuous operation. The optimum system for Malaysia's climate consists of 35 m² of evacuated tubular solar collector sloped at 20° and 3.5 kW of cooling capacity.

Ahmed Hamza et al. [64] report the performance of an integrated cooling plant including both free cooling system and solar powered single-effect LiBr/H₂O absorption chiller, which had been in operation since August 2002 in Oberhausen, Germany. A floor space of 270 m² is air-conditioned by the plant. The plant includes 35.17 kW of cooling absorption chiller, vacuum tube collectors' aperture area of 108 m², hot water storage capacity of 6.8 m³, cold water storage capacity of 1.5 m³ and a 134 kW of cooling tower. It is shown that free cooling in some cooling months could be up to 70%.

Izquierdo et al. [56] calculate the performance of a commercial 4.5-kW air-cooled, single effect LiBr/H₂O absorption chiller for residential use. Measurements are carried out over a period of 20 days. Results show that cooling power decreases with rising outdoor dry bulb temperatures. At outdoor temperatures from 308 to 314.3 K the chilled water outlet temperature in the evaporator climb to over 288 K. Qu et al. [70] develop an absorption system LiBr/H₂O for 16 kW of cooling water. They use parabolic collectors of 52 m² of area with heat exchanger and a pump for the recirculation of the working fluid. A burner for natural gas to provide heat in the absence of solar energy it is also present.

An experimental prototype of an absorption heat pump at single effect is developed and evaluated by Argiriou et al. [54]. This prototype is connected to a cooling tower and driven by solar heat at lower temperatures by means of solar collectors. The maximum value of COP equal to 0.74 is obtained. This system allows to obtain a saving of 20–27% of energy, compared to a conventional cooling system that uses a compression heat pump.

Joudi et al. [51] and Mateus and Oliveira [66] conduct an energy and economic analysis for SHC systems made with evacuated tubes solar collectors and absorption heat pumps at single stage.

Ibrahim et al. [50] simulate a solar-powered with a single-stage absorption system using LiBr-water as working fluid. A program is developed for the absorption system to simulate various configurations of the cycle using solar energy data of Antalya in Turkey. Thus, the effects of water input temperature to the system on COP and surface area of the heat pump are analyzed.

5.3. Two-effect absorption heat pumps with Li-Br/H₂O for solar cooling

Double-effect absorption cooling technology started in 1956 in order to develop system within a heat-source at higher temperatures. Tierney [81] develop a comparison among four systems with different chiller–collector combinations and at four different latitudes. The principal goal is to identify the combination that has the largest savings in primary energy for refrigeration demands of 50 or 100 kW: the combination of a trough collector with a double-effect evaporator is particularly effective. A smallest temperature of solar thermal cooling and heating system at Carnegie Mellon University in Pittsburgh, is studied by Qu et al. [70] through its design, installation, modeling, and evaluation. This system comprises a 52 m² of linear parabolic solar collectors and a 16 kW double effect water–lithium bromide absorption chiller. The absorption chiller is a dual natural gas burner to provide heat when solar energy is inadequate and is integrated with a cooling tower. Performance of the system is tested and the measured data are used to verify system performance models developed in TRNSYS. It is found that the solar COP of the overall installed solar cooling system is about 0.33–0.44 with the possibility to supply the 39% of cooling and 20% of heating energy for the building.

Tierney [72] compares four different systems with a collector of 230 m² and finds that the double-effect chiller with a trough collector

has the highest potential savings (86%) for a 50 kW of load.

Sumathy et al. [38] propose a two-stage H₂O/LiBr chiller for cooling purposes in south China: integrating a solar cooling system a value of 100 kW of capacity is obtained. The system has a nearly equivalent COP as the conventional cooling system, but at a 50% reduced cost.

Figueredo et al. [88] study the behavior of a H₂O/LiBr double-stage absorption chiller with 200 kW of cooling power. The system can operate in summer as a double-stage chiller driven by heat at 443 K from natural gas or as a single-stage chiller driven by heat at 363 K from solar energy, or simultaneously in combined mode. It can also operate in winter in double-lift mode for heating with a driving heat at 170 °C from natural gas.

Ezzine et al. [78] study a solar cooling integrated with absorption heat pump with two effect using H₂O/LiBr as working fluid.

The Technical University Graz, in Austria, has produced another prototype of absorption heat pump with a cooling capacity of 5 kW [78]. Although designed to be driven by the solar heat, the system can be operated by other renewable sources. The obtained COP is between 0.4–0.75.

Uppal et al. [75] develops an absorption heat pump using H₂O/LiBr as working fluid driven by solar energy and low cost. The purpose of this small capacity refrigerator is the vaccine storage in the remote locations of Third World countries.

Sierra et al. [76] realize an absorption heat pump with H₂O/LiBr as working fluid that uses solar energy for the production of cold. The COP varies between 0.24 and 0.28 while the minimum operating temperature of evaporation is 271 K.

Sozen et al. [77] develop a prototype of absorption heat pump with H₂O/LiBr as working fluid, designed to operate with a parabolic solar collector and with the inlet temperature of the generator of 363 K. Values of COP for cooling vary between 0.58–0.8 and in the range of 1.5–1.8 in the heating mode. Due to the minimum temperature of the evaporator 276 K, the system can be used for air conditioning and for the preservation of food.

Yaxiu et al. [83] carry out experiments for absorption heat pump with two stage: the temperature of heat source is 341 K compared to 373 K of traditional system. Infact, the difference in concentration of solution between inlet and outlet of the absorber is increased as the difference between the inlet and the outlet of the cooling water in the absorber increases. The performance of the evaporator is significantly improved due to the reduction of cold water temperature; also all system has a better efficiency. The maximum coefficient of 0.787 is measured and it is increased of 48.5%.

Calise et al. [84] realize an SHC system at high temperature with parabolic trough collectors and absorption heat pumps at double stage and an auxiliary heater powered by biomass.

5.4. Three-effect absorption heat pumps with Li-Br/H₂O for solar cooling

Li and Sumathy [85] underline the importance of the generator inlet temperature, chiller, collector choice, system design and arrangement, in the design and fabrication of a solar powered air conditioning system. Sriksirin et al. [86] discuss different absorption refrigeration systems and related researches. In this section, literatures pertaining to the improvement of absorption cooling systems, theoretical and experimental studies on solar absorption cooling, and finally, on subjects with a thrust on thermal storage integrated cooling systems are reviewed.

6. State of art about absorption heat pumps with NH₃/H₂O for solar cooling

Few works are present in literature about the absorption heat pumps with NH₃/H₂O as working fluid for solar cooling as shown in

Table 3

State of art of about absorption heat pumps with $\text{NH}_3/\text{H}_2\text{O}$ for solar cooling (a Flat plate collectors, b Evacuated tube collectors, c Trough collectors, d where not given, a collector efficiency of 0,5 has been assumed, e parabolic solar collectors).

References	Application	$Q_c[\text{kW}]$	$A_s[\text{m}^2]$	$\eta_{\text{cooling-heating}}$
[93] [91] [94] [77] [95] [78] [96]	Prototype chiller Space cooling/heating Prototype chiller Refrigeration/Heat pump	< 2.5		0.1–0.25 0.5
[97] [98,99] [59] [79] [100] [95] [101]	Space cooling Prototype chiller Prototype chiller Prototype chiller Space cooling	15 10 5 10		0.27 0.4–0.75
			60b	

Table 3.

Absorption heat pumps are discussed considering the η cooling-heating, the area of collector and the heat of evaporator. Prototype chiller is the most used application with $\text{NH}_3/\text{H}_2\text{O}$ pairs despite to $\text{LiBr-H}_2\text{O}$ working fluid. Space cooling/heating is another important application. Comparing Tables 2, 3, it is evident that ammonia-based working fluids are not the best choice for energy storage capacity and cycle efficiency.

Chinnappa et al. [91] develop a conventional vapor compression system cascaded with a solar-assisted $\text{NH}_3/\text{H}_2\text{O}$ absorption system. The hybrid system achieves a value of COP equal to 5, higher than a vapor compression cycle. The Technical University Graz (Austria) has produced another prototype of an absorption heat pump with ammonia/water as working fluid and with a cooling capacity of 5 kW. Although designed to be driven by the solar heat, the system can be operated by each type of renewable source. The operating temperature of the cold water varies between 283 and 293 K, while the COP is between 0.4–0.75.

The University of Applied Sciences in Stuttgart, Germany has developed several prototypes for air conditioning.

In one system, the cooling capacity of the single effect absorption heat pump is 10 kW and is driven directly by hot water from solar collectors without any thermal energy storage. The solution circulates through the use of a diaphragm pump, according the experiments conducted by Zetsche et al. [79].

Sozen et al. [77] realize a prototype of $\text{NH}_3\text{-H}_2\text{O}$ absorption heat pump: the system is designed to operate with a parabolic solar collector, having an optimum performance at generator inlet temperature equal to 363 K. The values of COP for cooling mode are in the range of 0.58–0.8 and for heating mode in the range of 1.5–1.8.

7. Thermal energy storage for solar cooling

One of the main problems using solar energy is the nonexistence of the sunshine at night and the variability of solar radiation during day time, so to avoid this problem, solar energy storage systems (SES) are used. These systems guarantee a continual supply of solar energy.

Thermal storage will also be beneficial if we can release surplus power during peak demand hours [102]. Thus, it is of great importance to design an efficient energy storage system that not only reduces the mismatch between supply and demand but also improves the performance and reliability of energy systems and plays an important role in conserving the energy. This section shows some solar thermal energy storage systems, discussing design criteria, innovative technologies and materials for heat transfer enhancement. In addition to thermal

storage, it is possible to have other systems: mechanical energy storage and electrical storage [102]. A detailed review about the design and economic aspects of the various thermal storage systems can be found in Kuravi et al. [103]. The materials used for solar thermal energy storage are classified into three main categories according to storage mechanisms: sensible heat storage, latent heat storage and chemical heat storage. Sensible heat storage and latent heat storage are physical processes while chemical heat storage is a chemical process.

Sensible heat storage is the most developed technology and uses a large number of low-cost materials [104] but it has the lowest storage capacity increasing the size of the system. Latent heat storage has much higher storage capacity, but poor heat transfer.

Chemical storage has the highest storage capacity, but whit the following problems: complicated reactors needed for specific chemical reactions, weak long-term durability (reversibility) and chemical stability.

Several methods of thermal energy storage for different temperature ranges have been discussed and reviewed [105–108]. Tyagi et al. [109] present a review of solar air heating systems with and without thermal energy storage. Table 4 shows a comparison about the different thermal energy storage, as sensible heat storage (solid and liquid phase) and latent heat storage (solid-liquid, liquid-gas, solid-solid phase). Vantages and disadvantages, the stored heat and the process technologies are presented, as shown in the following paragraphs.

7.1. Sensible thermal energy storage

When energy is stored or extracted by heating or cooling in a medium without undergoing phase change, it is called sensible thermal energy storage (SHS): they are simple in design, but larger in size and cannot store or deliver energy at a constant temperature. SHS system utilizes the heat capacity of materials during the process of charging and discharging. The amount of the stored heat depends on the specific heat, temperature change and amount of material. In general, the materials can be liquids (hot water, organic liquids, molten salts and liquid metals) or solids (metals, minerals and ceramics).

Water is the best SHS liquid available because it is inexpensive and has a high specific heat. However, above 373 K, oils, molten salts and liquid metals are used. The selection of the material depends on a few factors as the temperature, the value of heat capacity, the required volume and the cost.

For a proper performance of the system, the materials used in a sensible heat storage system must meet some requirements. According physical requirements they have a large heat capacity (to allow adequate storage size) and a large thermal conductivity (to allow easy charging and discharging processes). According technical requirements they have low vapor pressure, good chemical and physical stability and proper compatibility with container materials, avoiding corrosion phenomes. In addition, these materials must have low price and must be non-toxic and recyclable.

A advantage of sensible heat storage is its low cost, ranging from 0.05 US\$/kg to 5.00 US\$/kg, compared to the high cost of latent heat storage which usually ranges from 4.28 US\$/kg to 334.00 US\$/kg.

A common phenomenon of sensible thermal energy storage is thermal stratification, also known as temperature-ordered stratification [102]. The amount of stored energy is given by equation in Table 4.

7.2. Latent thermal energy storage

Latent thermal energy storage (LHS) using phase change materials (PCMs) provides high energy density storage due to the phase change of a material by freezing/melting.

In literature, there are many researches about the use of latent heat storage [110–117]. Kolb [118], Burkhardt et al. [119], Stekli et al. [120], Nithyanandam and Pitchumani [121], study solar systems with integrated latent thermal energy storage. The phase transformation of

Table 4
Comparison of different thermal energy storages.

Thermal energy storage	Phase transformation	Used material	Advantages	Disadvantages	Stored Heat	Process Technologies
Sensible heat storage	Solid	Table 3[125]Table 1[137]	Simple in design and relatively inexpensive Act as heat transfer surface and medium Large heat transfer area Non-toxic and non-flammable	Cost rises sharply for high temperatures, as storage tanks must be able to contain liquid at its vapor pressure Organic oils, molten salts and liquid metals use are limited because of their handling, containment, storage capacities and cost Larger amounts of solids are needed than using water, due to lower storing capacity than water Low storage capacity so the size system increases Larger volume and weight relative to latent heat storage Adjustment and control is variable and flexible	$Q = mcp(T_f - T_i)$ Eq.(1)[137]	Use of rock beds heated to different temperatures Installation of an underground tank using earth surrounding the tank as insulation Installation of water storage at a temperature a little above 373 K by using pressurized tanks Use of underground aquifers as natural water and thermal energy storage Application of solar ponds where heat is stored at the bottom of the pond employing large scale storage which exists in nature, such as Using underground aquifers which already contain water
	Liquid	Table 4[125]Table 1[137]	Simplicity Inexpensive, easy to handle, nontoxic, non-combustible and abundant High specific heat and high density Heat exchangers may be avoided if water medium is used for transport Natural convection flows can be utilized when pumping energy is scarce Simultaneous charging and discharging Adjustment and control is variable and flexible	Not corrosive Low or no sub-cooling Chemically and thermally stable No segregation Good compatibility with other materials except plastic at high temperature Recyclable High heat of fusion Availability in a large temperature range Higher storage capacity to sensible heat storage Work in nearly isothermal way Greater phase change enthalpy Good availability High heat of fusion High thermal conductivity (around 0.2 W/m K) Low volume change Availability in low cost Higher storage capacity to sensible heat storage Work in nearly isothermal way Sharp melting point	$Q = m[C_p(T_m - T_i) + \alpha m \Delta h_m + C_p(T_f - T_m)]$ Eq.(3)[137]	Finned tubes of different configurations in heat exchangers Bubble agitation Insertion of a metal matrix into the PCM PCMs dispersed with high conductivity particles Shell and tube Incorporation of high thermal conductivity enhancer: direct incorporation, immersion, microencapsulation (coacervation, suspension polymerization, emulsion polymerization, polycondensation, polyaddition) macroencapsulation Cascaded storage Integration with ejector cooling system
Latent heat storage	Solid-Liquid	OrganicTable 2[137]Tables 4, 5[138]	Paraffin Non Paraffin (Fatty acid)	Lower phase change enthalpy Flammability Poor thermal conductivity Low thermal conductivity (around 0.2 W/m K) Relative large volume change High cost Mildly corrosive		
	Liquid-Gas					
Solid-Solid		InorganicTable 3[137]Table 5[125]Tables 4, 5[138]	Metallics Salt Hydrates	Sub-cooling due to super-saturation Corrosive Phase separation Lack of thermal stability High volume change Nucleating agents needed, yet inoperative after repeated cycling Super cooling Segregation Materials degradation Low specific heat Decrease in heat of fusion after few cycle due to incongruent melting		
		EutecticsTable 4[137]Table 5[125]Tables 4, 5[138]	Inorganic-Inorganic Organic-Inorganic Inorganic-Inorganic Organic	Lack of currently available test data of thermo-physical properties Small latent heat to solid-liquid and liquid-gas		

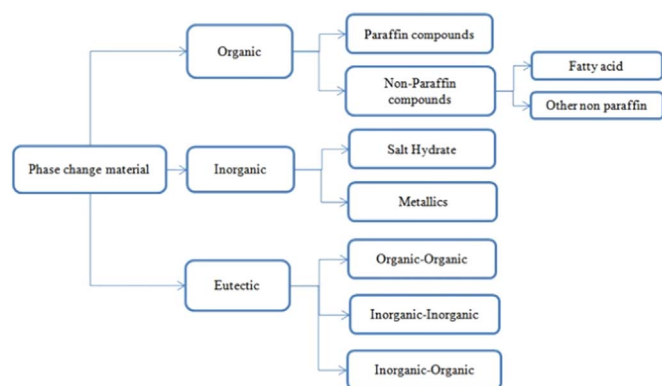


Fig. 7. Classification of latent heat materials in thermal energy storage.

the materials can be solid–solid, solid–liquid, or liquid–gas.

Transformation of crystalline nature from one to other will be observed in solid–solid latent heat storage material, whereas phase change of the material will be used to store thermal energy in other two methods of the latent heat storage. Solid–solid transformation has the advantage of small change in volume and greater design flexibility, but has small latent heat compared to solid–liquid and liquid–gas transformation which has larger latent heat and larger volume changes. Latent heat storage materials can be classified based on temperature, phase transition and used compounds. Among them the solid–liquid PCMs are the most suitable for thermal energy storage and comprise organic PCMs, inorganic PCMs and eutectics, as shown in Fig. 7.

Many researchers present reviews on low and high temperature phase change materials based on classification, need, selection criteria, long term characteristics, compatibility with heat exchanger materials, numerical models. However, very few studies are available for the energy analyses of PCM thermal storage integrated with solar thermal power plants [122]. In their behavior, initially, the PCM is in solid phase and when it reaches the melting temperature, the phase change starts and the temperature evolves at a constant value. As the interface evolves, the temperature of the material which has changed its phase, does not remain constant. Finally, the PCM is melted and in liquid phase [123]. For this mechanism, latent heat storage can work in a nearly isothermal way, due to the phase change mechanism, so it can be used in applications that require strict working temperatures. In general, latent heat storage presents advantages to sensible heat storage when used in applications where stabilization of temperature is desired or where heat or cold is stored with a small temperature change with high storage density. However, the main disadvantages of these systems are the low thermal conductivities, in the range of 0.2 W/(mK) to 0.7 W/(mK), lower phase change enthalpy and low phase change temperature. Some thermodynamic, kinetic, chemical and economic properties shown in Table 5 are need to be a desirable material.

Table 5 shows that thermodynamic properties (melting temperature in desired range, high latent heat of fusion per unit volume, high thermal conductivity, high specific heat and density, small volume changes at operating to reduce the containment problem, congruent melting) and chemical properties (complete reversible freezing/melting cycle, chemical stability, no degradation after a large number of freezing/melting cycle, no corrosiveness, no toxic, no flammable and no explosive material) are the most important for the selection of PCM respect to kinetic (high nucleation rate to avoid super cooling and high rate of crystal growth to meet demands of heat recovery from the storage system) and economic properties (large-scale availabilities and effective cost). Infact, the potential PCM should have a suitable melting temperature, desirable heat of fusion and thermal conductivity specified by the practical application.

The process to select a suitable PCM is very complicated: the potential PCM should have a suitable melting temperature, desirable heat of fusion and thermal conductivity specified by the practical

Table 5

Selection criteria for PCMs in solar refrigeration system.

Thermodynamic properties	(1) Melting temperature in desired range (2) High latent heat of fusion per unit volume (3) High thermal conductivity (4) High specific heat and high density (5) Small volume changes at operating temperatures to reduce the containment problem (6) Congruent melting
Kinetic properties	(1) High nucleation rate to avoid super cooling (2) High rate of crystal growth to meet demands of heat recovery from the storage system
Chemical properties	(1) Complete reversible freezing/melting cycle (2) Chemical stability (3) No degradation after a large number of freezing/melting cycle (4) No corrosiveness (5) No toxic, no flammable and no explosive material
Economic properties	(1) Effective cost (2) Large-scale availabilities

application. There are many measurement techniques, and differential scanning calorimetric (DSC) and differential thermal analysis (DTA) are most commonly used. The energy stored in latent heat storage medium is given by equation in Table 4. Latent heat storage, with higher heat storage density, small PCM volume and a relatively small temperature variation, has more attention in the past ten years. However, most PCMs have low thermal conductivities [124,125], which significantly increases the charging and discharging time for thermal energy storage. Methods of enhancing thermal and physical properties through incorporation of nano-materials encapsulation [126,127], shape stabilization and PCM slurries are also reviewed in large numbers. To enhance heat transfer in thermal energy storage systems, the insertion of high-thermal conductivity materials as metal fins, metal beads and metal powders is developed [128]. The encapsulations of PCMs, classified as micro-encapsulation and macro-encapsulation, are another option. Micro-encapsulation contains small PCM particles within a sealed, continuous matrix. This technique is widely studied and applied in textile industry [129], in district energy systems and in food industry [130], but the costs are higher compared to other storage methods. Different micro-encapsulation techniques are discussed by Hawlader et al. [131] and Boh and Sumiga [132]. Macro-encapsulation which uses rectangular panels, spheres and pouches (with diameter larger than 1 cm), is more common and applicable to both liquid and air as heat transfer fluids [133]. Although macro-encapsulation is potentially corrosive, it can avoid large phase separations, increase the rate of heat transfer and provide self-supporting structure for the PCM. Both micro-encapsulation and macro-encapsulation have strength, flexibility, corrosion resistance and thermal stability [134]. Shape-stabilised PCMs, in which the PCM is dispersed in another phase of supporting material to form a stable composite material, have an increasing attention due to their large apparent specific heat, suitable thermal conductivity, good performance of multiple thermal cycles over a long period [135].

7.2.1. Organic PCMs

A phase change material which contains carbon atom is known as organic PCM and it is classified into paraffin and non-paraffin. PCMs with the general chemical formula C_nH_{2n+2} are categorized under paraffin, where the heat of fusion and melting point increases with the increasing of carbon atom number. Non paraffin PCM is the compound which contains functional groups such as alcohols, glycols, esters and fatty acids. Organic PCMs are available for a wide range of temperatures which are stable till 573 K. The advantages of using organic PCM are no tendency to segregate, chemically stable, high heat of fusion, no tendency of super-cooling and compatible with all containers except plastic at high temperature. Some of the demerits are low thermal

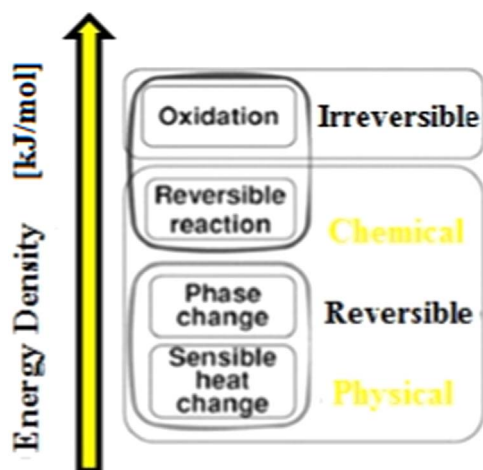


Fig. 8. Comparison of energy density between the different thermal energy storage methods [136].

conductivity, high cost, sometimes flammable and mildly corrosive. Organic materials can melt and solidify several times without phase segregation and degradation of their latent melting heat; they are usually not corrosive.

7.2.2. Inorganic PCMs

Inorganic PCMs are materials which consist of salt hydrates, nitrates and metallic and can also be used for higher temperatures up to 1773 K. Inorganic PCMs are superior in terms of low cost, easy availability, sharp melting point, high thermal conductivity, high heat of fusion and lower volume change. It is associated with demerits such as super cooling, segregation, materials degradation, corrosion of heat exchangers, low specific heat and decrease in heat of fusion after few cycles due to incongruent melting [68]. These kind of PCMs have a double volumetric latent heat storage capacity (250–400 kg/dm³) than the organic compounds (128–200 kg/dm³).

7.2.3. Eutectics PCMs

Eutectic PCMs are mixture of two or more compounds at a particular percentage of composition; they melts and freezes without segregation because they freeze into a crystals, without the separation of components. On melting both components liquefy simultaneously, giving less probability of separation. The compounds can be of any combination like organic-organic, inorganic-inorganic and organic-inorganic.

7.3. Chemical thermal energy storage

Thermal energy can also be stored using the reversible chemical reactions. Fig. 8 shows that they present higher energy density than other thermal storage methods; sensible heat change has the lower energy density. Other advantages are the higher ambient temperature storage and the possibility of heat pumping and long distance transport.

Technical compatibility of this method is yet to be proven.

However, chemical storage has not yet been extensively researched, and its application is limited for same problems: particular reactors for specific chemical reactions, chemical stability; however, the system provides a wide range of operation temperatures and lower heat losses [137]. Three different modes can be used: reversible reactions, thermochemical pipeline energy transport and chemical heat pump storage. Thermal energy is stored and retrieved by breaking and reforming the molecular bonds through reversible chemical reactions [102].

Suitable materials for chemical heat storage can be organic or inorganic. Several criteria must be considered during the design of chemical heat storage: excellent chemical reversibility, large chemical

enthalpy change and simple reaction conditions.

8. Conclusions

Renewable energy sources have considerable interest due to their promising advantages and in this contest cooling technologies based on solar energy are promising technologies for the future.

A detailed literature about absorption heat pumps integrated in solar systems and thermal energy storages to produce cool energy is presented.

These systems are characterized by environmental sustainability and energy efficiency.

PV and PV/T solar systems can be used and from other studies it is evident that absorption heat pumps have gained considerable attention among researches; also thermal energy storages are important to take maximum advantage of solar resource, increasing the cooling availability and improving the overall performance.

Sensible, latent and chemical heat storages are available. PCMs in the latent heat storages are the preferable choice.

Future researches should be about the development of affordable thermal storage systems, refrigeration systems of solar panels and new working fluids that are environmentally friendly and require low operating temperatures.

Also it is necessary to increase the market penetration of solar cooling. Infact, there are many pilot and demonstrations experiences in solar cooling system. A suggestion is to optimize this system reducing capital and operating costs finding the optimal number of the effects in absorption system. The combined solar cooling and PV/T systems and single-effect absorption chillers may be more competitive in both economic and technological aspects. Furthermore, it is highly suggested to establish optimal operational control strategy so as to realize smooth switch between the solar cooling system and the auxiliary energy system. Also, researches on the integration and control of various schemes for multiple uses (cooling, heating, water heating, and power generation) may produce synergic efficiency enhancement.

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