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Overview of working fluids and sustainable heating, cooling and power generation technologies

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Abstract

Dependency on energy is much higher than the past and it is clear that energy is vital for a sustainable and safer future. Therefore, urgent solutions are required not only to increase share of renewable resources but also more efficient usage of fossil fuels. This could be achieved with innovative power, air conditioning and refrigeration cycles utilising 'long-term sustainable' (LTS) fluids, especially air, water and CO_2. In the article we provide a rational approach to the future use of working fluids based on our interpretation of the available technical evidence. We consider it self-evident that volatile fluids will continue to play major roles in cooling and power generation, however, new technologies will be needed that optimise energy efficiency and safety with minimum environmental impact. Concordantly we discuss the past and current situation of volatile fluids and present four innovative technologies using air/water cycles. Study results showed that there is a rapid development in heating, cooling and power generation technologies those use water/air as working fluid. These technologies demonstrate a potential to replace conventional systems, thereby to contribute to global sustainability in near future. However, further development on LTS fluids and materials also process intensification and cost reduction are vital parameters for future advancement of these technologies.

Keywords: long-term sustainable fluids; sustainability; air conditioning; refrigeration; power generation

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1 INTRODUCTION

Like the majority of scientists, the authors accept the scientific evidence that human activities are causing global warming. Despite the uncertainty that still remains about the sensitivity of the atmosphere to greenhouse gas emissions, notably CO_2, which affects the onset and frequency of adverse weather events, we consider that new cooling, heat pumping and power generation technologies to reduce greenhouse gas emissions need to be developed now. Delaying until the anticipated effects of global warming are pronounced might be too late.

Recognising that global energy demand is rising but the world can burn only 20% its established fossil fuel reserves by 2050 if global warming is not to exceed 2°C represents a major threat to the future of all humans [1]. The present rate of fossil consumption means that this will be achieved by ~2030.

While fully agreeing that the greenhouse gases must be urgently reduced, we believe that considerable confusion has been

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created over the past 15 years, not least as the result of political lobbying. In the article we provide a rational approach to the future use of working fluids based on our interpretation of the available technical evidence…We have no remit from either the fluorinated fluid or the 'natural' fluid industries to defend their positions. While we consider it self-evident that volatile fluids will continue to play major roles in cooling and power generation, new technologies will be needed that optimise energy efficiency and safety with minimum environmental impact. This article explores available options.

Refrigeration and air conditioning (AC) currently contribute to global warming directly by the release of high GWP hydrocarbon fluid (HFC) refrigerants and indirectly by carbon dioxide emissions from fossil fuel power stations producing electricity to drive compressors. Yet as more people around the world quite properly aspire to the living standards of the developed world, the demand for cooling will increase. Ironically, higher global temperatures will drive the demand for AC and thus the demand for electric power, which, if satisfied by fossil fuels, increases global, warming in a positive feed-back loop.

Organic Rankine cycle (ORC) systems, although less numerous than cooling units, in many cases depend upon similar fluorinated fluids. By optimising heat recovery from low temperature sources, including combined heat–power (CHP) and thermal solar energy, they help to reduce dependence on fossil fuels. Nevertheless this benefit needs to be compared to global warming generated by fluorinated working fluid leaks.

Primary objective of this article is to investigate the latest advancements in the fields of heating, cooling and power generation systems. Furthermore, evaluation of the historical development and hazards of process fluids used in these technologies were discussed. Accordingly, it was proposed to interpret the potential for replacing chemical fluids with natural-sustainable fluids (i.e. air and water) in near future.

1.1 The past

Even in antiquity refrigeration and AC was valued. The Egyptians produced ice by exposing shallow trays of water overnight in locations where a breeze would cause evaporation resulting in freezing. The Babylonians, Romans, the Persians and Chinese transported ice from mountainous regions and stored it in ice houses prior to distribution. Seasonal ice storage become of increasing importance until the introduction of mechanical refrigeration in the last quarter of the 19th century. In the 1870s the UK was importing ice from as far away as North America and Norway. British stately homes often had ice houses, many of which still exist, where ice harvested from lakes in the winter was stored for summer use. The Babylonians cooled their houses by splashing water over the walls. Islamic gardens created a millennium ago incorporated fountains to create cool areas for the comfort of their wealthy owners. Water clearly was the first refrigerant [2].

In 1805 Oliver Evans, an early American steam engineer and inventor, was the first to propose the vapour compression cycle, with ether as the working fluid, but did not build a working device. Pioneers of early refrigeration included the following:

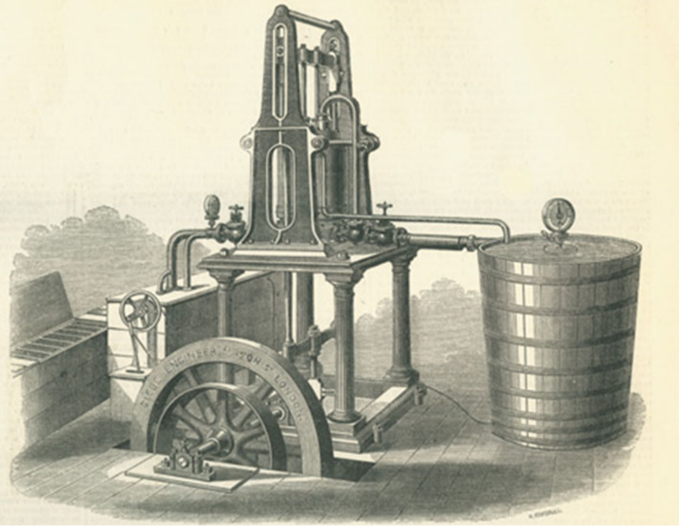


Figure 1. *Harrison's ice-making machine. System provides cooling by evaporating the ether at a low temperature [3]. This concept constitutes the basics of today's heat pump refrigeration cycles.*

In 1835 Jacob Perkins was the first who patented the vapour compression for a practical refrigeration system.
In the early 1850s Australian James Harrison was the first to produce a practical commercial refrigeration machine producing ice and using ether as working fluid (Figure 1). Units were rapidly adopted by breweries in Australia and Britain.
In 1851 John Gorrie, an American medical doctor, developed an ice-making machine providing cold air for cooling fever patients. Intriguingly, he combined a/c with coolth storage and was the undisputed father of AC, but his work was way ahead of its time. AC attracted little attention until the seminal work of Carrier in the early 20th century.

Truly modern industrial refrigeration began in the early 1870s with the development of ammonia vapour compression systems by Carl von Linde, a technology that has endured and has been progressively developed to the present day.

Although the first carbon dioxide refrigeration was explored around the same time as Linde's ammonia development, the technology began to make an impact from 1890 onwards when British manufacturer J.E. Hall started manufacturing industrial units. These were especially favoured for refrigerated food ships because of the low toxicity and non-flammability of CO_2 compared to ammonia and other refrigerants (SO_2, methyl chloride and hydrocarbons) available in late 19th century and early 20th century. In the 1930s 80% of the British chilled food fleet used CO_2 as the refrigerant.

With the increasing availability of electric power and of small electric motors, SO_2 based refrigerators were developed for domestic and small commercial applications. Their popularity grew after the WW_1, especially in the USA, but not-infrequent leaks led to adverse press reports. General Motors, the owner of Frigidaire, recognised that further expansion of refrigeration needed new and safe refrigerants. Engineer Thomas Midgley, chemists Albert Henne and Robert McNary, tasked with finding replacements, scanned the chemical literature and decided that the CFCs and HCFCs, discovered by Belgian chemist Frederick Swarts in the 1890s, provided the right combinations of boiling points and safety. Du Pont and General Motors set up Kinetic Chemicals in 1930 to manufacture the new fluids. CFCs R114, R11 and R12 were among the first to be manufacture followed by R22. These non-flammable, low toxicity fluids allowed the refrigeration to develop rapidly, especially after WW_2 when rising standards, first in the USA and then in the rest of the developed world increased demand for food refrigeration and AC. Not surprisingly the same trend is being seen in developing world since cooling demand and living standards are inter-related.

After nearly 30 years of near-exponential growth after WW_2 and against a background of increasing environmental awareness, the fate of CFCs in the atmosphere started to be questioned [4, 5]. Lovelock showed that CFCs persisted in atmosphere [6]. In 1972, against a background of, the CFC/HCFCs producers themselves began to question what was happening to the CFCs/HCFCs being freely released in to atmosphere? [7]. The answer was that they had no idea since there appeared to be no natural sinks for these compounds. The fundamental break-through was the landmark paper by Rowland and Molina suggesting that CFC and HCFC omissions could result in the destruction of stratospheric ozone, which shields the biosphere from harmful UV radiation, caused considerable concern [8]. The industry jointly funded independent academics to check the Rowland and Molina thesis…The intention was to find the truth, not just excuses to rubbish the thesis. Simultaneously the industry looked for alternatives to CFCs/HCFCs, which had similar performance, efficiency, low toxicity and non-flammability. From these programmes the HFCs, notably R134a emerged. By 1980 atmospheric science and the modelling of the effects of CFCs/HCFCs indicated there was a potential problem, but the effect would take decades to have a serious impact. Although the manufacturers were prepared to replace CFCs/HCFCs with non-ozone depleting HFCs these results combined with the global recession removed the political will to legislate against ozone depleting substances.

The situation changed in 1985 with discovery of the so-called 'ozone hole' by the British Antarctic Survey during the Antarctic spring [9], which was subsequently shown to be the result of chlorine containing compounds condensing on stratospheric clouds trapped in the polar vortex. As the sun rose after the polar winter the clouds evaporated releasing a chlorine pulse and hence causing a rapid decrease of ozone over the South Pole. Subsequent scientific studies proved that man-made chlorine compounds were largely responsible.

Under the auspices of the Montreal Protocol (1987) UN member states agreed to limit the manufacture and release of ozone depleting substances, notably CFCs/HCFCs. The Protocol also made provision for ongoing scientific work to understand the severity of the problem and to allow restrictions to be tightened. By the mid-1990s it was clear that to prevent continuing stratospheric ozone depletion CFCs/HCFCs would need to be phased-out completely. The Protocol was amended; first CFCs would go because they had highest ozone depletion potential, followed by the HCFCs. Developed countries, which were more economically able make the transition, were required to phase out more quickly than the poorer countries. Europe unilaterally banned the manufacture of CFCs after 1995. HCFCs, notably R22, were banned as a refrigerant after the end of 2014, including the recycling of existing material.

HFCs replaced CFCs/HCFCs in many applications combining comparable efficiencies, non-ozone depletion, low toxicity and non-flammability.

1.2 Unravelling confusion…

To answer to the question posed in title of reference 5 is 'yes', the HFCs have solved ozone depletion caused by CFCs and HCFCs, although it will take until ~2100 for the 'ozone hole' to disappear. But the HFCs themselves have now come under increasing pressure as potent global warming gases. The new question now is 'what replaces the HFCs?' In the authors' view trying to answer this question has caused considerable confusion since science, technology and politics have become muddled.

How much do the HFCs contribute to global warming? The scientifically authoritative sources of information are the IPCC reports on global warming published by the UNEP [10]. At present HFCs contribute ~1% to global warming, which appears 'trivial' compared to the major greenhouse gases, notably CO_2 and methane. Their 15% per annum growth is the problem, which if unchecked would result in an estimated 0.5 K increase in global warming by 2100. HFCs also contribute to global warming indirectly when used as refrigerants via the CO_2 emitted by fossil fuel power stations to supply the power to generate the electric power to drive refrigerators and air conditioners. Obviously replacements for HFCs should not result in significantly lower energy efficiencies otherwise the contribution of fossil-fuelled cooling equipment to global warming will increase, not decrease. If hydrofluorocarbon, such as R245fa, is used to generate electric power from 'waste' heat or in a CHP unit then it reduces CO_2 emissions, provided these are greater than the global warming caused by HFC leaked from equipment.

1.3 'Chemical' vs 'natural' refrigerants?

While supporting the move from HFCs to so-called 'natural' fluids to reduce potential global warming, we consider that these have issues, which although well-known and not denied by industry, are not being properly communicated to the general public. In particular the use of term 'natural' is misleading, especially since it is often contrasted with 'synthetic' or 'chemical' as opprobrious descriptors for HFCs. To combine the low toxicity and non-flammability of the HFCs with low environmental impact and long-term sustainability the choice of working fluids is restricted to water, air and CO_2. Clearly, this is relevant to domestic applications and has informed the technologies described in this article. For applications where inventories are small or in large installations, where engineering supervision is continuous and public exposure limited, then hydrocarbons and ammonia are acceptable. We suggest that 'natural' fluids might be more accurately as 'long-term sustainable' (LTS) fluids.

In both the technical and non-technical literature, fluorine-containing (HFC) refrigerants are increasingly referred to as 'chemical' or 'synthetic' refrigerants in contrast the so-called 'natural' refrigerants [11]. In part at least, this is a reaction against the Chemical Industry which is perceived to be contaminating the environment in its unremitting pursuit of profit despite the fact that it an essential contributor to the living standards of developed nations. 'Chemical' is now seen by some as being 'bad' and is contrasted with 'natural', which implies good. Even a leading UK national newspaper, The Daily Telegraph, noted for its sceptical articles on the existence of man-made global warming [12], in 2006 pointed out that 'everything is made of chemicals, and so claims that products are 'chemical-free' are not true' [13], yet in 2012, published an article entitled 'The green guide to chemical free beauty' [14] extolling the merits of 'natural' products, which chemist recognise as being chemicals. If a Telegraph, with its reputation for quality journalism, can publish articles that differ about the meaning of 'chemical' then the confusion between so-called 'chemical' and 'natural' refrigerants is perhaps not surprising. The scientific community acknowledges that communicating clearly with the general public is essential; this requires a consistent terminology, and resisting its distortion for commercial or ideological reasons.

In the context of refrigerants what is meant by the term 'chemical'? The major fluorochemical fluids are R32 (CH_2F_2), R125 (CF_3CF_2H), R143a (CF_3CH_3), R134a (CF_3CH_2F), R227ea (CF_3CHFCF_3), R152a (CHF_2CH_3) and R245fa ($CHF_2CF_2CH_2F$). The 'natural' refrigerants are water (R718), air, R714 (ammonia), carbon dioxide (R744), R290 (propane, C_3H_8), R600a (methylpropane), R600 (*n*-butane, $CH_3CH_2CH_2CH_3$), *n*-pentane, R601a (2-methylbutane) and cyclo-pentane [15]. Whether they are HFCs or 'natural' refrigerants, all can be synthesised by chemical reactions and all can undergo chemical reactions. In other words they are self-evidently all chemicals. Patent [16] refers, correctly in our view, to these compounds, whether fluorine-containing or not, as chemical refrigerants to distinguish them from thermoelectric devices, a distinction which is valid. But the distinction between 'chemical' refrigerants and 'natural' refrigerants is technically meaningless in terms of their properties.

Water, air, carbon dioxide, some hydrocarbons and ammonia are 'natural' in the sense that they are present in the biosphere. But this, in itself, does not necessarily make them desirable as refrigerants. Sulphur dioxide could be described as 'natural', and, pedantically at least, this might be extended to dichlorodifluoromethane (CFC-12), which has reportedly been detected in volcanic gases [17]. Both are now rightly rejected as refrigerants, although both were used in the past.

Ammonia and carbon dioxide used as refrigerants are manufactured from methane ('natural' gas) in large chemical plants, so they are just as much 'synthetic chemicals' as the fluorocarbons. The point is that by calling carbon dioxide and ammonia 'natural' in contrast to the 'synthetic', fluorocarbons makes a generic distinction in terms of their origin is also meaningless. If the carbon dioxide is recovered from biomass fermentation, for example bioethanol manufacture, then it might reasonably be termed 'natural', or at least 'biochemical'. Perhaps a better term is 'sustainable'. Ammonia obtained from putrefying animal wastes would be 'natural', although we would question whether the process would be economic. More sensibly, ammonia might be manufactured from hydrogen obtained from the electrolysis of water using renewable energy and atmospheric nitrogen via conventional technology. Even more exciting, is the potential for low temperature ammonia production [18]. In principle this approach is sustainable, although it involves a 'chemical synthesis', so the ammonia thus produced should be described as 'synthetic' or 'chemical' not 'natural'.

The HFCs are typically obtained from natural gas purification plants and oil refineries, which are chemical plants primarily operated to produce refined fossil fuels and chemical industry feedstocks. If the hydrocarbon refrigerants were simply recovered by distillation from natural gas then they could with reasonably be described as 'natural'. But when fossil fuels are finally phased-out then they will no longer available from this source. To be 'sustainable' they might be obtained from biomass processing [19]. The hydrocarbons thus obtained would be 'synthetic chemicals' and could not honestly be described as 'natural', but they would be sustainable.

Methoxymethane (dimethyl ether, CH_3OCH_3), already manufactured on a substantial scale as an aerosol propellant, is a promising low global warming refrigerant. We cannot find any reports of biological sources, so it cannot be regarded as 'natural', in the sense of occurring in nature. Although clearly 'synthetic', it is being developed as a second generation bio-fuel [20], especially for use in low-pollutant diesel engines and thus will be available as a 'sustainable' but 'synthetic chemical' refrigerant.

Some may consider the above discussion is pedantic suggesting that 'natural' is just a convenient label to identify a group of refrigerants that have low direct environmental impact. Although lacking precision this might be perhaps acceptable as 'jargon' for those working in the refrigerants field. But this would be to miss the point. Bearing in mind that the scientific and technical communities are often criticised for not communicating their work clearly to the general public we should remember the adjective 'natural' conveys a specific meaning to the non-technical general public, essentially as defined by The Oxford Dictionary; 'natural' as follows: 'existing in or derived from nature; not made or caused by humankind'. The term 'natural' applied to refrigerants is an obfuscation. At present all fluids marketed as refrigerants, whether fluorochemical or so-called 'natural', are derived from petrochemical feedstocks, none of which are sustainable. The ultimate target must be 'sustainable', albeit 'synthetic', refrigerants manufactured from bio-renewable resources by environmentally low-impact processes based on green chemical technologies, consistent with the ethos of circular manufacturing technology [21]. We suggest calling these products 'LTS' refrigerants, or more broadly working fluids since they might be employed in ORC systems; these are listed in Table 1.

1.4 Hazards

Starting in the 1930s, the desire for low toxicity and non-flammability drove the move away from the LTS fluids to the CFCs and HCFCs. By returning to these fluids means accepting the hazards they entail, which are not trivial. Ammonia, a refrigerant that has been used since the beginning of modern refrigeration in the 1870s, still causes serious accidents and fatalities. A listing of 99 refrigerant incidents compiled by the European Fluorocarbons Technical Committee (EFCTC) from March 2006 to October 2013 records 981 injured, 236 severely injured and 95 fatalities with 16 772 evacuated [22]. By far the greater majority resulted from ammonia leaks. Three incidents resulted from hydrocarbon leaks (1 injured, 11 severely harmed and 1 death). Five CO_2 incidents were recorded although one had no data (40 injured, 1 severely harmed, 200 evacuations). One fluorocarbon leak was noted (1 injured, 1 death). Since the data originated from an organisation with an explicit interest in promoting fluorocarbons against LTS fluids, a selection of the links to the original data sites were checked and found to be correct. Using the search terms 'ammonia + accident' an Internet search generated additional, more recent examples of ammonia releases causing problems. 'hydrocarbon + accident + refrigerant' generated a recent report by the London Fire Brigade concerning the fire hazard of domestic freezers related especially the flammable cyclo-pentane blowing agent. EU and American legislation restricts the hydrocarbon charges in appliances with heat exchangers in rooms to a maximum of 150 g. This information reinforces what was already known, that is ammonia and hydrocarbons are potentially hazardous, especially when used on the large scale without adequate supervision. The Singapore government is sufficiently concerned to restrict their applications [23]. We are not arguing for the phasing out ammonia and hydrocarbon, merely suggesting that their range of applications will be limited, because with tens of millions of installation world-wide accidents will inevitably happen.

Table 1. *Long-term sustainable fluids.*

Chemical structure	Chemical name	ASHRAE number	Normal BP (°C)
	Air		
H_2O	Water	R718	100
NH_3	Ammonia	R414	−33.4
CH_3CH_3	Ethane	R170	−88.6
$CH_3CH_2CH_3$	Propane	R290	−42.1 ± 2
$CH_3CH(CH_3)CH_3$	*Iso*-butane (methylpropane)	R600a	−11.7
$CH_3(CH_2)_2CH_3$	Butane	R600	0 ± 1
CH_3OCH_3	Methoxymethane (dimethyl ether)	R170E	−24
$CH_3(CH_2)_3CH_3$	*Normal*-pentane	R601	36.1 ± 2
$CH_3CH(CH_3)CH_2CH_3$	*Iso*-pentane (2-methylbutane)	R601a	27.7
$CH_2CH_2CH_2CH_2CH_2$	*Cyclo*-pentane	R407c	49

While accepting that hydrocarbons are acceptable for applications where <150 g charge is adequate, and, with ammonia, for big installations that can be properly monitored by appropriately skilled engineers, we suggest for larger domestic, commercial and industrial applications, which are not routinely monitored, then safer refrigerants are essential. With the phase-out fluorinated refrigerants because of environmental concerns then fluid choice is driven back to water, carbon dioxide and possible air. In looking for technologies, whether AC, refrigeration, heat pumping or low temperature power generation/CHP the authors have therefore focused on water and air based systems, which in some cases can be advantageously coupled with vapour compression transcritical CO_2 systems.

Examples of cooling/AC, heat pumping, power generation and energy storage systems are presented in the following sections. Figure 2 summarises these innovative technologies using air or water as LTS fluids.

2 DEW-POINT COOLING

Market research completed in 2013 on the usage of AC indicated the industry gains £55 billion in revenues globally. China alone accounts for £18 billion of this sum, while the UK accounts for £600 million. Mechanical vapour compression systems dominate the cooling sector making up 80% of the above market share [24]. However, evaporative cooling (EC) market is expected to experience fast growth over the next 10 years from £5.5 billion in 2013 to £20 billion in 2024. [25] This is due to the increasing attention gained by EC using the natural refrigerants water and air. Use of water as cooling medium and air as a heat transporter (air/water cycles) is a promising alternative to electrically powered heat pumps.

The basic idea of AC has been refined through centuries of evolution. The ancient Egyptians hung wet mats in their doors and windows in order to allow wind to blow through them to cool the air. This can be considered the first attempt at AC. Mechanical fans were introduced in the 16th century to provide air movement, and by the 19th century cooling towers with fans were introduced to blow water-cooled air inside factories. Evaporative coolers are the innovative technology of the 20th century [26].

EC basically adds water vapour to the air and can be considered a simple, efficient and cheap method to decrease the temperature. However, direct EC (DEC) is a cause of concern given that the resulting high humidity both reduces thermal comfort and causes mold growth that could cause several allergic problems and diseases (Figure 3). In addition DEC has low efficiency in humid climates, as only limited amount of water could be added to the air. Desiccant systems can be integrated to evaporative coolers to overcome this problem.

However, necessities of desiccant regeneration also complex system design are the main barriers for this cooling method to compete with heat pumps. Alternatively to DEC, indirect EC (IEC) technology has developed based on novel core (heat exchanger) technology, enabling to cool air without moisture addiction (Figure 3).

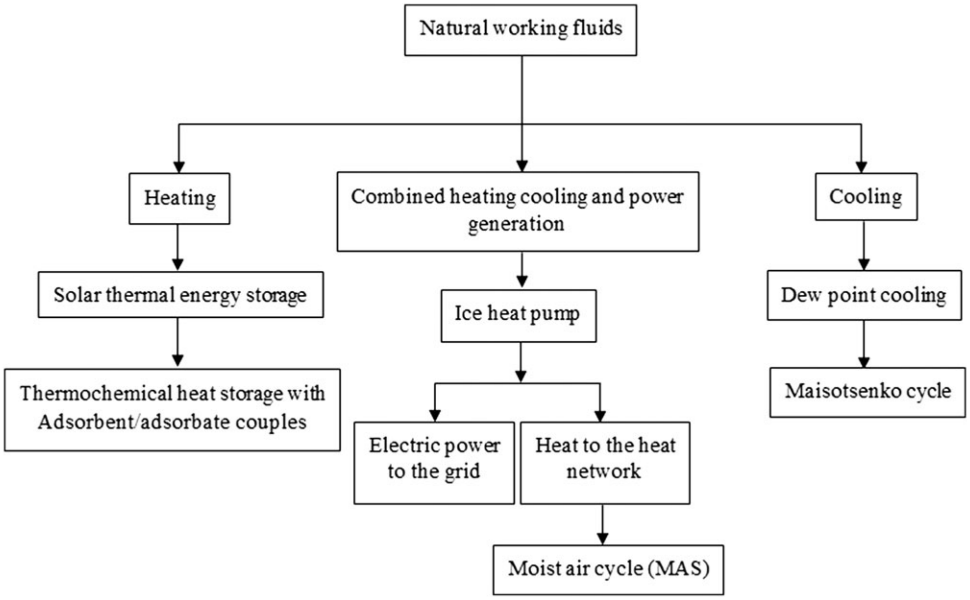


Figure 2. *Classification of the sustainable heating, cooling and power generation technologies proposed within the study.*

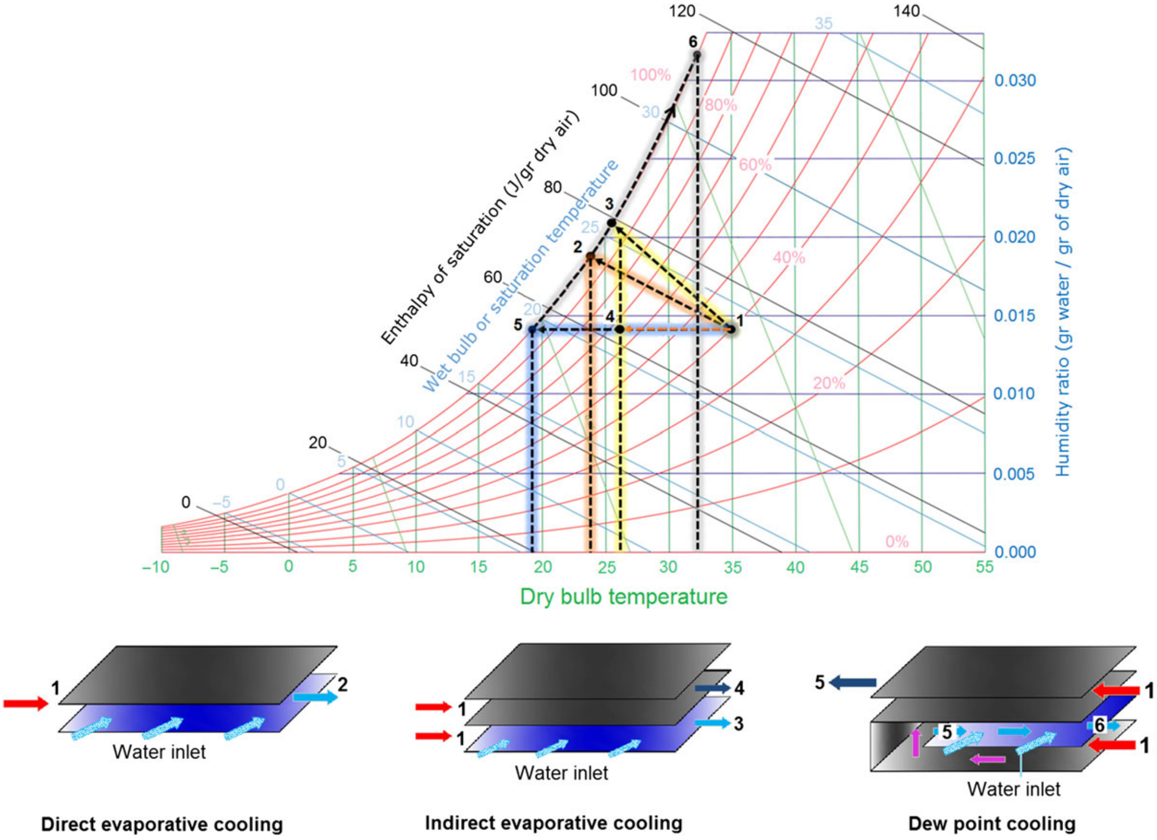


Figure 3. *Evaporative cooling technologies. Figure describes three different methods of air cooling and the description of the process of each method in psychometric diagram.*

With IEC, a secondary (scavenger) air stream is cooled by water in wet channel. The cooled secondary air stream goes through a core, where it cools the primary air stream flowing in the dry channel. IEC does not add moisture to the primary air stream. Both the dry bulb and wet-bulb temperatures are reduced. However, IEC systems still have technical drawbacks including the limitations in air temperature drop and the large dependency on the ambient air conditions, where the lowest temperature that could be attained is the intake air wet-bulb temperature. In addition, efficiency of IEC is 60–70% whereas DEC efficiency is usually 90%. This is because in DEC cooling is achieved with adding moisture to the air and new temperature is found on wet-bulb gradient. In IEC new temperature is found on dry bulb gradient as a result of a temperature drop without moisture addiction.

In order to overcome the stated drawbacks of IEC, a breakthrough step was taken in the last decade and dew-point EC has been developed based on Maisotsenko cycle (M-cycle) [27]. M-cycle based dew-point cooling is a revolutionary thermodynamic process that utilises the psychometric energy (or the potential energy) available from the latent heat of water evaporating into the air and uses atmospheric air as a renewable source of energy [28, 29]. The cycle is well-known in the AC field due to its potential of dew-point EC. The M-cycle uniquely combines the thermodynamic processes of heat transfer and dew-point EC by utilising the psychrometric renewable energy available from the latent heat of water evaporating into the air. In one way it enables the product (i.e. air or any fluid) temperature to approach the ambient air dew-point temperature. On the other way it acts as a humidifying recuperator consecutively. Hence, it can be used as cooler as well as humidifying heater simultaneously in HVAC and cooling applications [30].

The performance of any EC system is largely dependent on the structure and design of the heat and mass exchanger. Thereby modifying the exchanger of the IEC system, air could be cooled below its wet-bulb temperature and towards the dew-point temperature [31] (Figure 3), which lies behind the remarkable performance of dew-point coolers.

A performance comparison between open cycle desiccant cooling, direct contact EC and dew-point cooling systems was provided in Table 2. It is seen from the table that dew-point coolers could operate as efficient as evaporative or desiccant coolers without increasing the moisture content of product air.

Authors carried out several studies on dew-point cooling technology [35, 36] and reported that counter-flow exchanger for M-cycle dew-point cooling provides greater (around 20% higher) cooling capacity, as well as greater (15–23% higher) dew-point and wet-bulb effectiveness than cross-flow exchanger, when equal in physical size and under the same operating conditions. However, it is indicated that cross flow system, however, had better (10% higher) energy efficiency (COP) [37, 38]. Theoretically with dew-point coolers, product (primary) air could be cooled until saturation line, which will significantly increase efficiency up to 90%. Dew-point cooling can be considered a break-through technological advancement as it provides larger intake-supply air temperature difference than any other EC method without any moisture addiction to supply air.

A dew-point evaporative cooler is introduced to the market by Coolerado Corporation using M-cycle [39], which is basically benefitting from latent heat of evaporation of water to cool the product air up to dew point. Their system uses a cross flow heat exchanger core, has COP value of 16 and a payback period of <2 years. As an example of the latest status of cooling cycles with air/water couple, this system will be a revolutionary step towards green energy. Future developments will be heat exchanger design and material for further enhancement of dew-point cooler efficiency. Currently single intake—counter flow and double intake—cross flow are favourable core designs [40]. On the other hand in terms of material, sandwich aluminium-foil/fibre [36, 37] and cellulose fibre with water proof coating on one side are promising heat exchange surface materials for effective dew-point cooling performance [41].

3 COMBINED HEAT AND POWER GENERATION

CHP system is a promising way of utilising solar energy and waste heat from industry, power plants and other commercial buildings. CHP is a proven technology with technical, economic and environmental benefits using the low-grade heat for both electrical and thermal power supply. Authors agree that the key to reduce future energy consumption-fossil fuel dependency lies on maximum utility from low-grade heat. According to Bradley [42], every year 10 GW of potential power is squandered as waste heat from industrial processes—enough to light 10 million homes. However, the high installation cost of CHP systems is an obstacle and government stakeholders have a key role in this just like other renewable energy applications. As an example, the Danish government mandated expansion of CHP as a national policy beginning in the 1980s, requiring grid operators to pay for the power generated at a set rate [43]. The guaranteed ability to sell electricity stimulated the construction by private entities of relatively small-scale CHP plants. The same strategy lies behind the rapid growth of wind and solar

Table 2. *Thermodynamic performance assessment of evaporative cooling systems [31].*

Study	System type	Energy efficiency (%)	Exergy efficiency (%)	COP
Kanoglu *et al.* [32]	Open cycle desiccant-based evaporative cooling system	93.6	36.5	0.345
Taufig *et al.* [33]	Direct contact evaporative cooling system	–	38	–
Calıskan *et al.* [34]	Dew-point evaporative cooling system	90	19.1	0.19

power in Denmark and in Germany as well. In Germany CHP contributed 13% of electricity generation in 2009. The German government has a target to increase CHP to 25% of generating capacity by 2020. Furthermore, USA is targeting 50% increase in CHP capacity by 2020, which would correspond to around 12% of US generating capacity [44].

With CHP co-generation systems, heat that might be lost as a by-product of electricity generation is captured for power generation also space and water heating. Locally supplied electricity incurs lower transmission losses than the national grid, which losses ~40% of its supply. Payback periods of four to 10 years are possible [45]. CHP can also produce a 30–50% reduction in carbon dioxide emissions, as well as, be incorporated with absorption chillers or desiccant coolers for space cooling called 'tri-generation'.

ORC has been widely studied for CHP systems as it is suitable for small and large scale heat and power generation with utilising low-grade heat. However, health and environmental concerns on refrigerants will be a barrier for further development and implementation of ORCs. On the other hand moist air cycles for CHP, will be a new trend as they use natural refrigerants, work in lower pressures and enable to recover high amount of heat as a result of moisture condensation. Buyadgie [46] newly reported a developed CHP system using moist air and called 'Solar Low-Pressure Turbo-Ejector M-Power System' (SLTE-MPS). This system replaces the compressor with an ejector and utilises a serial HMX core, produced by Coolerado for AC through M-cycle for equalising counter flow pressures at the same atmospheric or sub-atmospheric level. It is claimed that the system converts solar thermal energy into electrical power with a thermal efficiency of 30–40%, which is 11–18% for steam–water Rankine cycle. Buyadgie says that: 'In the Brayton power cycle, mechanical compressor consumes useful work. When ejector replaces compressor, the system's efficiency increases 2–2.5 times since ejector does not consume work and serves to optimise pressure after the turbine' [46].

Another promising technology proposed by the authors for refrigeration and AC as an alternative to the conventional heat pumps is ice heat pump using open air/water cycle. The system uses air compressor and expander units and a water atomising nozzle. Water, which is injected at the expander inlet of the heat pump, is converted into ice at the outlet of the expander. The use of air and water, as natural refrigerants, will result in a highly efficient and environment friendly heat pump system for ice and heat production.

Figure 4 shows the ice heat pump working principal. The ice heat pump system is an energy saving device. It harnesses heat from ambient air, water vapour/steam under low temperatures to solidify and release a large amount of latent heat. The heat is converted to mechanical work through the expander to offset compression work, thereby improving the COP of the heat pump.

In the system ambient air enters the air compressor and it is compressed to a high pressure. The high pressure/high temperature air is then passed through the heat exchanger/condenser unit and releases heat that could be used for space heating. At the inlet of the expander unit, water is injected using an atomising nozzle. The air/water–vapour mixture is then expands through the expander unit producing ice. The expander outlet is connected to an ice–water separator/tank. An ice agitator powered by an electric motor could be used to break the ice into ice slurry. The ice slurry could be used for space cooling or refrigeration.

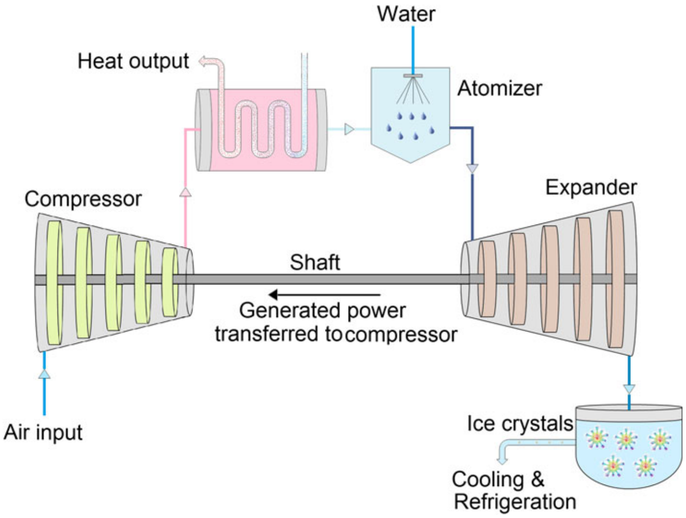


Figure 4. *Schematic diagram of ice heat pump.*

The proposed technology uses air and water as the working fluids. The utilisation of the sensible heat of dry air and sensible heat/latent heat of water would maximise the absorption of energy from ambient air and water. The water phase change contains a large amount of energy and therefore the ice heat pump will have a great advantage compared to conventional heat pumps using HFCs.

3.1 What is the benefit of CHP?

CHP can offer a variety of economic benefits for large energy users. Considering the sharply increasing demand of electricity, local power generation with CHP could be reducing the stress on electricity grid. Additionally it can provide security of supply, making energy go further, through more efficient use of fuel—regardless of whether the fuel is renewable or fossil [47]. Alternatively, reduction in the cost of energy with CHP will improve the competitiveness of industry and business, helping alleviate fuel poverty and lowering cost in delivery of public services [48].

3.2 Do we have the luxury to ignore the heat demand?

The supply of heat is largely ignored in the energy and climate change debate, despite heat representing nearly half the world's final energy consumption. According to IEA report [49], in 2009, heat represented 47% of final energy consumption, compared with 17% for electricity, 27% for transportation and 9% for 'non-energy' (raw material usage of fuel) use. Oil, coal and gas account for more than two-thirds of the fuels used in meeting this significant demand for heat. Currently thermal power plants operating based on Rankine cycle, only convert the 30% of fuel energy to electricity as a final product meaning that rest of the energy is wasted as low-grade heat. Conversely, the potential of CHP lies behind providing the maximum benefit from the energy source and delivering not only electricity but also heat, which allows efficiency to reach 90–95% also to reduce the environmental emissions [50, 51]. According to a report by Pöyry Energy Consulting [52] for Greenpeace, the energy produced by power plants that provide both heat and electricity could be almost tripled in the UK. So-called CHP plants are far more efficient than conventional power stations because they harness heat that is normally wasted, by piping it to industrial or domestic users with heat networks. Heat networks have a key role in order to benefit from CHP technology, and many sources of heat that are currently not being used. They provide a means of transporting waste heat from industrial processes and some commercial buildings.

4 HEAT NETWORKS: THE KEY TO SAVE THE WASTE HEAT

Heat networks are gaining attention in the last decade as they act as a bridge between the waste heat sources (e.g. industrial and power plants) and the residential sites [53–55]. Heat networks are commonly used in Eastern Europe, Germany, South Korea, USA, Canada and Scandinavia. Approximately 61% of the customers in Denmark, receive their heat via heat networks [44].

Heat networks will prove to be the key for waste heat recovery in the future. Similar to the electricity grid, effective heat networks will allow central production–distribution, and will bring many advantages such as balancing the heat-supply demand, reducing the heating costs, investment costs (on heating systems), CO_2 emissions and wasted energy [56–59]. However, heat networks should be cost effective including low investment and operational costs in order to easily integrate with other systems. Water is mainly used as the heat transfer fluid, which requires a high pumping pressure. High pressure pumps would be expensive to run and also water pumping could results in leakage problems. On the other hand, heat transport with air is not feasible as a result of low specific heat of air. According to authors using moist air which will significantly reduce the required duct size and allow long distance effective heat transport called 'Moist air system' (MAS) (Figure 5) will be more practical. Assume that Q kW 497 heat is transferred from heat source A to the heat sink B with a well-insulated (Qloss ~ 0 kW) duct line by using (i) dry air as heat transfer fluid and (ii) humid (moist) air as heat transfer fluid. The heat transport capacities of dry air and humid air were analysed considering several parameters including density, pressure, enthalpy and humidity. Results of analysis revealed that the required duct size (diameter) for the transport of equal amounts of heat is much lower when moist air is used as the heat transfer medium than when dry air is utilised. An example of transporting 1 kW heat from A to B, at the same air velocity, the required duct diameter for dry air is found to be ~210 mm whereas only 14 mm is required for moist air.

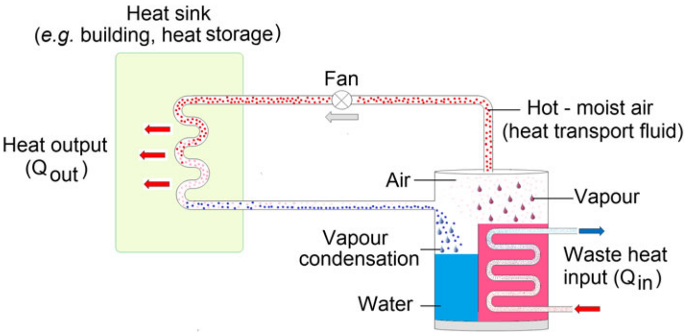


Figure 5. *Moist air system. Figure describes the working principal of MAS. Accordingly waste heat from any kind of heat source (e.g. industrial plants, solar energy) is supplied to the system for evaporating the water for humidifying the air until the saturation point. Hot- moist air transports the heat from the heat source to the heat sink (e.g. building and heat storage) and both sensible heat (temperature) and latent heat (vapour condensation) of humid air is transferred.*

4.1 Moist air system: a better way to transport the heat

MAS is a unique and novel heat transfer system, which utilises a network of highly insulated small flexible ducts containing flowing air and moisture as the heat transfer medium. Recovered waste heat as well as the generated useful heat will be efficiently transported to the CHP plant and customer building network via MAS. This will allow the harness of low-grade waste heat (100–150°C) released from waste incineration, biomass and industrial plants for heat production and electricity generation, thereby making more efficient use of waste heat recovery (Figure 6). Localised waste heat-driven CHP-MAS system will be future's promising technology for sustainable heat and power generation at reduced cost.

MAS system would be effective for transferring waste heat from different locations to buildings. Solar heat could easily be utilised using MAS as medium for connecting different devices such as hot water tanks and power generation units operating at low temperature heat. Alternatively MAS system could be integrated to HVAC systems used to supply heating and cooling via radiation panel, fan coil etc. in buildings and would be compatible with the building structure as it does not require a large space. Additionally heat transfer coefficient (850–1700 W/m^2K) [60] for moist air and water are in a close approximation, therefore, usage of moist air instead of water in central heating applications does not bring any disadvantage/obstacle in terms of overall heat transfer to the building from the radiator.

MAS system has the potential to replace the conventional heat transport methods especially in multi-storey buildings and towers due to the given advantages and its light, low cost, low pressure and flexible nature.

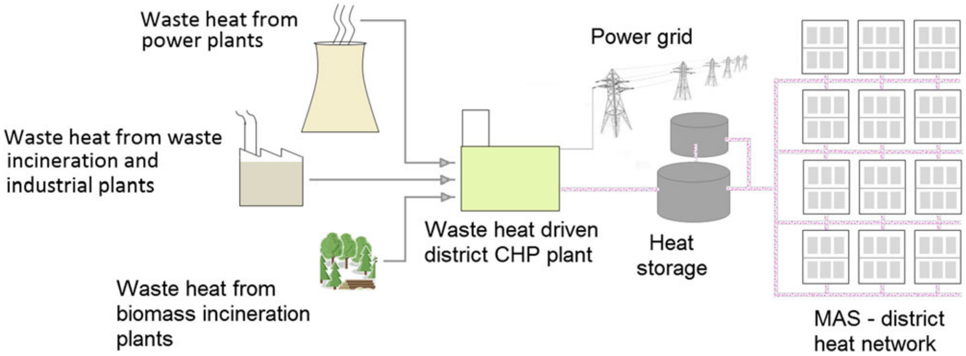


Figure 6. *Schematic diagram showing MAS—heat networks between waste heat sources, centralised CHP plant and residential site.*

5 ENERGY STORAGE: PATHWAY TO SOLAR HEATING

In order to fully benefit from renewable sources, technological development in renewable energy industry leads to energy storage which is crucial for bringing a balance between supply and demand.

The main drawback of renewable sources is that they are not steady and climatic conditions are difficult to determine. Although it is clear that we already developed technologies to harvest power from renewables, we are still struggling to store and accumulate these energies. Unfortunately weather conditions are changing continuously and giving unpredictable outputs. Therefore to harvest energy generated as a result of natural events, we must urgently develop energy storage technologies in order to contribute to our sharply rising renewable energy demand. We can save the solar energy in summer to use it in winter or during daytime to use it at night. This condition will both compensate the mismatch between supply and demand, as well as, dramatically reduce the payback period of renewable energy technologies [61].

Electrical storage is on the target in the last decade especially for bringing the PV technology to a cost effective level. In addition there are an increasing number of large scale electricity storage applications especially in hydroelectric form in Northern Europe, China, Japan and USA and in many other countries. Compressed air storage also has been gaining attention and currently small and large scale compressed air storage systems are available in the market. On this context Lindey [62] critically investigated the possible ways to storage of electrical energy and looked at a number of technologies for storage in the form of potential energy (hydroelectricity), pressure (compressed air), kinetic energy (flywheels) and with using batteries or ultra-capacitors.

Although some significant advancements have been achieved on storing electricity, unfortunately thermal energy storage is highly ignored. However, as mentioned previously, thermal energy constitutes almost half of world total energy demand. Still the combustion of natural gas, coal and oil are primary drivers for space and water heating purposes in buildings. Usage of these fuels should be restricted only for power generation considering their high carbon emissions, less availability and high energy potential. Utilising fossil fuels for domestic heating (low temperature) purposes is briefly wasting their potential by using them to generate low quality energy. Consequently, in developed countries the highest energy consumption is in building sector with 27%. Also 70% of atmospherical emissions including greenhouse gas sourced from the building sector [63]. This problem requires an immediate solution which is linked to storage of solar energy.

Sensible heat storage (SHS) is a mature technology for short term storage and latent heat storage (LHS) is showed a potential for balancing the mismatch between day and night as well. However, with these technologies it seems highly unlikely to reach the goal of long-term heat storage due to the high heat loss and low heat storage densities. As seen from Figure 7, sorption energy storage materials have energy storage density in the range of 800–1600 MJ/m^3 whereas for LHS and SHS materials storage density varies between 200–1100 MJ/m^3 and 100–600 MJ/m^3, respectively. This condition indicates a major advantage of THS of lower volume requirement when compared to SHS and LHS. This is important to reduce the space requirement in buildings for heat storage applications.

A possible way for seasonal storage of solar energy will be the thermochemical heat storage (THS) based on vapour adsorption–desorption of zeolites, silica gels and salt hydrates (Table 3). Due to the nature of these materials, as long as they kept hygro-thermally insulated in dry form they are able to store heat independent of the time without any heat loss. Thereby solar energy could be used for drying these materials in summer for generating heat in winter (Figure 8).

THS materials have ~6–8 times higher storage density over SHS, and two times higher over LHS materials (Figure 7). However, in THS vapour or moist air transfer is the prime mover which is not an issue in sensible or LHS. This condition brings a requirement for innovative reactor design in order to provide effective vapour diffusion through the adsorbent [65].

Additionally regeneration temperature is another important parameter for efficiently drying the adsorbents with solar energy in summer. Although zeolite and silica gel have satisfy most of the requirements to be a candidate material, they seem highly unlikely to regenerate with solar energy as zeolite requires 250–300°C and silica gel requires 150–200°C for complete regeneration. Thereby salt hydrates came into question as some salt hydrates ($CaCl_2$, $LiNO_3$, LiBr, MgCl, $MgSO_4$, LiCl) demonstrated remarkable adsorption properties since they are highly hygroscopic and generate heat due to vapour adsorption [66, 67]. However, the drawback of salt hydrates is that they turn into an aqueous solution as a result of vapour adsorption therefore a host matrix is required to hold the solution. The host matrix has significant importance on the overall adsorption mechanism (Figure 9). The matrix serves to both hold the adsorbent and prevent dispersion of it. Also some of the host matrices can enhance HAM transfer due to the increased surface area and increased performance of the salt/sorbate reaction. The sorbate (water vapour) sorption process contains two main mechanisms, (i) a chemical reaction between the salt and sorbate and (ii) liquid absorption.

Corrrosivity of some salts (i.e. LiCl and LiBr) is a major problem in THS applications and needs to be considered in

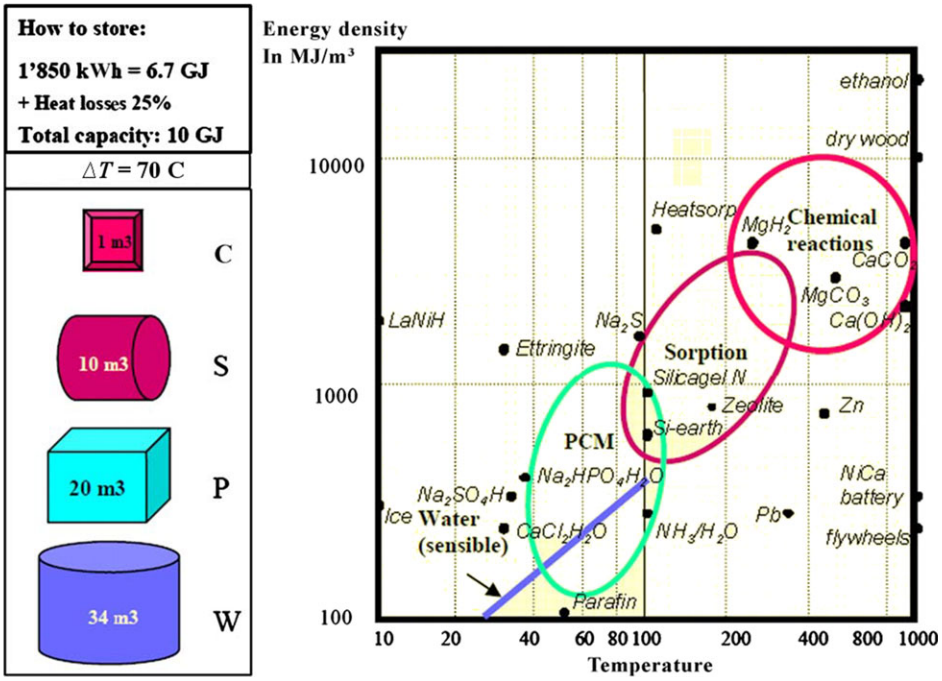
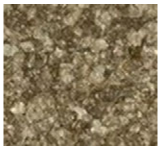


Figure 7. *Comparison of energy storage densities of energy storage methods. Adapted from Bales [64].*

Table 3. *Comparison of promising candidate materials for thermochemical heat storage.*

Evaluation criteria	 Silica gel	 Zeolite	 Vermiculite–$CaCl_2$
Regeneration temperature	H	VH	L
Multi-cyclic ability	M	L	H
Heat storage density	M	H	M
Ease of handling	H	H	M
Toxicity	NT	NT	VL
Corrosivity	NC	NC	VL
Moisture uptake capacity	H	H	H
Adsorption temperature	M	H	M
Cost	H	H	M
Density	H	H	L

Several parameters should be considered for determining the best candidate thermochemical heat storage material. The table compares the most important parameters of zeolite, silica gel and V–$CaCl_2$ directly affecting heat storage performance. VH, very high; H, high; M, medium; L, low; VL, very low; NT, not toxic; NC, not corrosive.

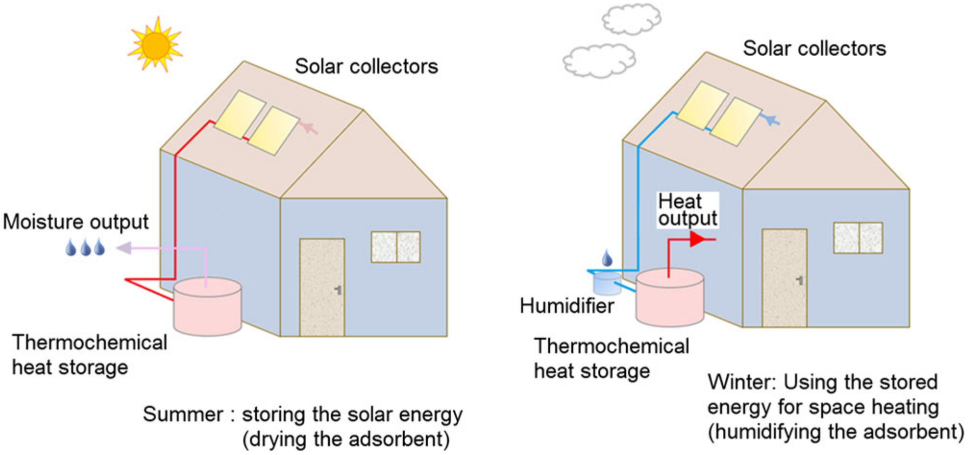


Figure 8. *Schematic diagram of seasonal thermochemical heat storage. In summer solar energy is used to dry the adsorbent (THS material). In winter ambient air is pre-heated with solar energy (collectors) and humidified. Humid air enters the THS and heat is generated due to vapour adsorption. Hot air is used for space heating. This system presents a simple and inexpensive method for long-term storage of solar energy.*

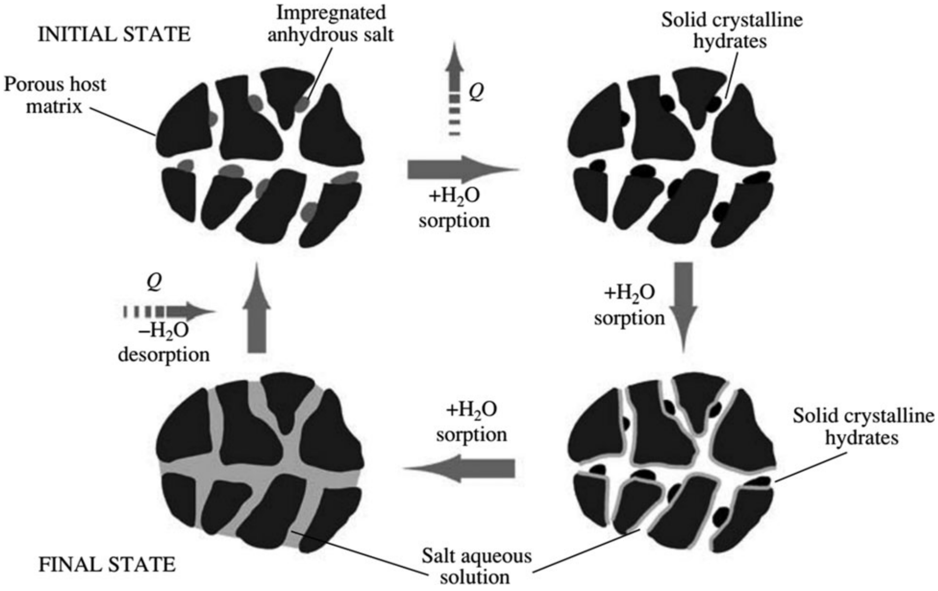


Figure 9. *Water sorption mechanisms on salt [68, 69].*

selection of THS material. Corrosion in THS reactors negatively affect the heat storage performance as it deteriorates the salt matrix. In addition it reduces the reactor life time. Therefore, if corrosive THS materials are used, it is important to select polymer based reactor material (i.e. polypropylene) instead of metallic materials (i.e. aluminium) to avoid corrosion.

Our research showed that vermiculite could be a promising candidate with its nano-porous nature, low cost, low density, high permeability and high mass uptake. We have tested several nano-composite adsorbents based on salt hydrate impregnated vermiculite. Results revealed that composite $CaCl_2$–vermiculite has a great potential as it provides 30°C temperature lifting of air, heat storage density of 250 kWh/m^3 and has a regeneration temperature of 80°C which is achievable with solar energy in summer conditions [65, 67]. The composite matrix is also cost effective as unit price is found as \$540/m^3.

Future developments on THS will focus on reactor design, enhancing heat heat/mass transfer and innovative integration of solar collectors and heat storage systems. This heat storage method demonstrated a potential to be a solution for long-term heat storage which will enable us to efficiently utilise solar energy as well as any kind of waste heat.

A future target for reduction of building sourced energy consumption and greenhouse gas emission should be achieving centralised large scale, MW level heat storage systems, which will collect and distribute the heat to the buildings via heat networks by utilising moist air system.

6 DISCUSSION

Future energy security and minimal environmental impact of energy generation and consumption could be achieved with focusing on innovative technologies using 'natural' fluids for power, heat and coolth generation. We have presented the historical evolution of working fluids with providing technical evidence in order to overcome the confusion on their environmental impact. Later we focused on four innovative technologies using air/water. From our point of view, volatile fluids will continue to play major roles in cooling and power generation in the future. However, presented new technologies using air/water couple will be the key to optimise energy efficiency–safety also optimal usage of volatile fluids with minimal environmental impact.

According to the study results, dew-point evaporative cooler for AC, ice heat pump for combined heating, cooling and power generation and THS for solar driven space heating are key technologies for achieving global sustainability in close future. Yet these systems need further improvement, mainly on process and material optimisation. Also water usage is another drawback for these technologies, particularly for the use in places where there is water scarcity.

Current study also emphasises the importance of heat networks for more effective use of renewable sources, industrial waste heat and CHP plants. In the last decade, there is an increasing interest on district heating system where hot water is carried via underground piping systems from a heat source (i.e. waste heat of industrial plants and geothermal) to a site for buildings' space heating and hot water supply. However, the major problems in such applications are high capital cost, complexity and difficulty of installation of the district heating pipe networks. Present study suggests a promising opportunity of using hot moist air in heat networks in district heating systems. Lower installation costs, lower operational costs due to minimal need for pressurisation, also easier installation of MAS due to the reduced ducting size represent major advantages for the use of it in district heating systems as well as in tall buildings for heat distribution. Development of light, flexible and low cost moist air pipes having low heat loss coefficient constitutes the main field of future research in this area.

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