# A review of chemical heat pumps, thermodynamic cycles and thermal energy storage technologies for low grade heat utilisation

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## HIGHLIGHTS

► The review of various thermal technologies for the utilisation of under exploited low grade heat.
► The analyses of the absorption and adsorption heat pumps possibly with performance enhancement additives.
► The analyses of thermal energy storage technologies (latent and sensible) for heat storage.
► The analyses of low temperature thermodynamic cycles to maximise power production.

## ARTICLE INFO

## ABSTRACT

A major cause of energy inefficiency is a result of the generation of waste heat and the lack of suitable technologies for cost-effective utilisation of low grade heat in particular. The market potential for surplus/waste heat from industrial processes in the UK is between 10 TWh and 40 TWh, representing a significant potential resource which has remained unexploited to date. This paper reviews selected technologies suitable for utilisation of waste heat energy, with specific focus on low grade heat, including: (i) chemical heat pumps, such as adsorption and absorption cycles for cooling and heating; (ii) thermodynamic cycles, such as the organic Rankine cycle (ORC), the supercritical Rankine cycle (SRC) and the trilateral cycle (TLC), to produce electricity, with further focus on expander and zeotropic mixtures, and (iii) thermal energy storage, including sensible and latent thermal energy storages and their corresponding media to improve the performance of low grade heat energy systems.

## 1. Introduction

Since the onset of the 'Great Recession' [1] which began in December 2007, a decrease in ecologically friendly investments is generally envisaged, particularly after the withdrawal of Canada from the Kyoto treaty. However, a recent survey by Ernst & Young has reported that many firms, such as BHP and Rio Tinto, have actually increased their ecologically friendly investments [2] as the falling price of renewable energy and the rising price of crude oil have made energy efficiency and clean energy more attractive. This finding is in agreement with another survey of over 500 large companies conducted by Carbon Disclosure Project [3], which claimed that 59% of emissions-reducing investments made so far have shown a three-year payback period on average. These reports indicate that investments to improve energy efficiency can result in significant monetary savings.

A major cause of energy inefficiency is the generation of waste heat and the lack of waste heat utilisation, particularly low grade heat. The temperature range for low grade heat sources is typically between ambient temperature and 523 K [4,5], and such low grade heat is especially abundant in industry as by-products. The market potential for surplus/waste heat from industrial processes in the UK is between 10 TWh and 40 TWh [6–8]. This represents a significant potential resource which has remained under-exploited to date, mainly because of the cost of obtaining useful exergy and energy out of low grade heat. Law et al. [9] claimed that the complete recovery of waste heat would be higher than the output of many of the renewable energy sources currently used in the UK, and that a large amount of low grade heat is available in the process industries as water from cooling towers with temperature between 308 K and 328 K, or as flue gas or vapours from stacks with a larger temperature range, between 303 K and 523 K. Opportunities to deploy low grade heat (up to 523 K) in industry are plenty as indicated in Fig. 1 which presents the range of heat supply required by industrial processes in producing different products within the EU-27. Although low grade heat generally exists in the form of waste heat from the process industries, other examples

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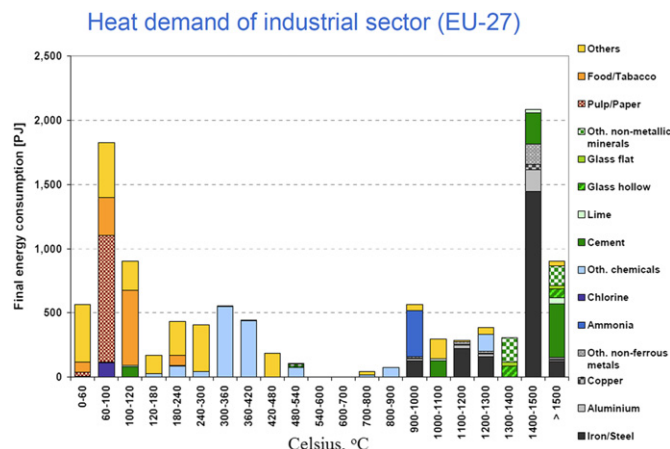
**Fig. 1.** Temperature distribution of industrial heat in EU-27 in 2009 [10].

of low grade heat including renewable energy resources, e.g. solar, are available within the temperature range. It is worth mentioning that low grade heat technologies can be practically applied to other sectors such as automobile and HVAC (heating, ventilation and cooling) systems. Thus, the employment of low grade heat presented beyond the scope of the process industries should not be overlooked.

The scope of low grade heat utilisation is very broad (the scope of heat utilisation that encompasses a wider range of temperatures as shown in Fig. 1 is even broader). It covers heat exchangers, heat pipes, heat pumps, energy storage, heat recovery, process intensification and optimisation, etc. The authors are currently working on a technology roadmap on thermal energy management with an intention to cover the aforementioned technologies. The roadmap will be in much greater detail, presenting a more holistic view of the current state and the future direction of thermal related technologies across all temperature ranges. This paper will however focus on three distinct areas, i.e. thermal energy storage, chemical heat pumps (thermo-chemical energy conversion) and thermodynamic cycle (thermo-electrical energy conversion) in order to summarise and capture the spread of the challenge that lies ahead in low grade heat ($<$523 K) thermal energy management.

## 2. Low grade heat technologies

### 2.1. Chemical heat pump

A chemical heat pump in principle consists of a condenser, an evaporator and one reactor (with a generator) or two reactors (or adsorber/absorber), and is used to upgrade and store thermal energy,

particularly low grade heat, via the reversible reaction between chemical substances without chemical consumption or production. Wongsuwan et al. [11] and Fadhel et al. [12] state that a chemical heat pump can either involve gas–liquid absorption process [13,14] or solid–gas adsorption process. Adsorption chemical heat pump [15] can be further classified into chemisorption chemical heat pump [16–19] or physisorption chemical heat pump [20–23]. As a sub-set of adsorption, chemisorption is driven by a chemical reaction occurring at the exposed surface. The strong interaction between the adsorbate and the adsorbent creates an electronic bond, either ionic or covalent. In contrast, physisorption is a result of the van der Waals force where the interaction energy is very weak, with a 0.5 eV difference in binding energy. A chemical heat pump is more environmentally friendly than the relatively more conventional vapour compression heat pumps, as the compressor component consumes more electrical energy. For more information on vapour compression heat pumps, refer to Reay [24]. A chemical heat pump involves endothermic desorption and exothermic adsorption/absorption processes. It is desirable to have an adsorbent–adsorbate pair or an absorbent–absorbate pair with high heat of adsorption/absorption to create a more compact system. The adsorbent/absorbent reacts to the heat and releases reactive gas (adsorbate/absorbate) which goes through the pipeline and reaches the user site. At the user site, heat can be produced due to the exothermic adsorption/absorption processes (or condensation process).

Scientific literature on fundamental principles, classifications, working modes and economic analysis of chemical heat pumps, for example [11,12,15,25–27] to name but a few, has affirmed that chemical heat pump is a sustainable technology to recover low grade heat (including geothermal energy) and supply energy during heat-demand period. Chemical heat pump technology can work as a stand-alone technology or can be integrated into a combined heat and power (CHP) system to form tri-generation, also sometimes referred to as combined cooling, heating and power (CCHP) systems. Tri-generation or CCHP is still a new scientific frontier. Research on tri-generation mainly focuses on absorption cycles [28–31] rather than adsorption cycles [32]. Reay [33] discussed the practicality of further industrial applications of heat pumps. As noted by Chua et al. [34], the absorption cycle has been operating in industries [35–37], however the commercial applications of the adsorption cycle are much more uncommon [38], and only limited to Japan [39] although the theory and lab-scale models have been extensively studied and demonstrated [40–44]. This section will discuss both adsorption and absorption cycles in detail.

#### 2.1.1. Adsorption cycle (gas–solid)

Adsorption cycles can be classified into multiple-bed cycles and thermal wave cycles [45]. Fig. 2(a) and (b) respectively illustrates
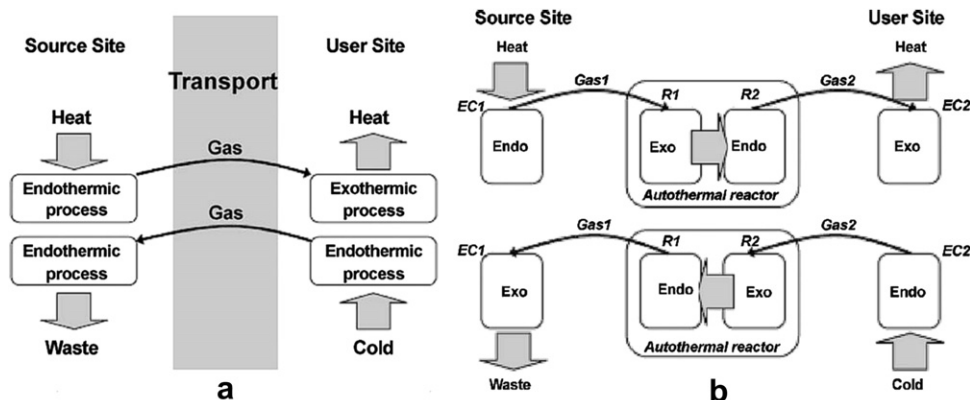


**Fig. 2.** (a) The single effect adsorption cycle, and (b) the cascade adsorption cycle for heat transportation [50].

a single effect adsorption cycle (the number of effects indicates the number cooling a single cycle can achieve) for low grade heat transportation and a multiple-bed cycle (also may be referred to as a cascade cycle) which is a combination of two or more adsorption cycles. The multiple-bed cycle has the potential for wider applications due to its more flexible heat source temperatures, ranging from 313 K to 368 K [46–49]. Both beds are at different temperatures but remain isothermal.

Figs. 3 and 4 show a few multiple-bed cycles, where the coefficient of performance (COP) and the complexity of multiple-bed systems increase with the number of beds [45]. It is worth noting that the more complex the system, the higher the upfront cost. Therefore, the adoption of multiple-bed cycles has to strike a balance between COP performance and system complexity. For more complex multiple-bed cycles, refer to the work of Kang et al. [51]. The thermal wave process, as illustrated in Fig. 5, shows how a thermal front can move through an adsorbing bed and a desorbing bed in a cycle. At the point where the thermal front is about to break through, the flow direction of the heat transfer fluid is reversed, which effectively switches the function of the beds from adsorbing to desorbing and vice versa [52].

Ma et al. [50] investigated more than two hundred reactive salts applicable for adsorption cycles. The common characteristics [53] of an adsorbent bed include:

- low thermal conductivity, leading to longer periods of adsorption and desorption, hence larger equipment (such as the adsorber column) is needed to achieve the required reaction time;
- mass transfer rate that depends on the adsorbate flowing through the adsorbent particle and through the adsorbent bed;
- adsorption performance is governed largely by the available surface area;
- distribution of temperature and adsorbate concentration are influenced by the bed porosity; and
- the increase of porosity reduces the thermal conductivity and mass transfer resistance, but increases the adsorption period.

Adsorbents with thermal stability, high thermal conductivity, high adsorption capacity, and low cost are desirable in practice. On the other hand, non-corrosive, non-toxic, thermally and chemically stable gasses with high latent heat are preferable characteristics of adsorbates. A few examples of adsorbent–adsorbate pairs and their corresponding heat of adsorption are presented in Table 1.

According to Ma et al. [50], adsorption systems have two main shortcomings, namely the amount of energy required to transport the gas and the intermittent heat transportation process. Heat transfer can be improved via 3 different methods (as summarised in Table 2):

(a) preparation of a composite reactant/adsorbent combined with a heat transfer promoter which has high thermal conductivity;
(b) addition of metals or carbon fibres into a bed; and
(c) integration of a reactant into a heat exchanger.

In method (a), expanded graphite, normally used to promote heat transfer, is prepared by impregnating with an inorganic salt solution, followed by drying and calcining to deposit the salt inside the pores of the expanded graphite [56]. This can improve thermal conductivity by up to 10 times, which is larger than that of the bed packed with untreated salt particles [57]. The thermal conductivity of expanded graphite can also be improved by compression [58,59]. In general, metallic foams and zeolites are suitable to be used as composites [60,61]. If adsorbents are insoluble in water, resin can be used as a binder to bond the adsorbent with expanded graphite [62].

In method (b), insertion of fins with a small volume fraction of 0.01 into a packed bed can increase the effective thermal conductivity by six times [63] while insertion of a carbon fibre brush with volume fraction of 0.05 can increase it by four times [64].

In method (c), integrated reactors of adsorbent layers packed between the fins of the heat exchanger have been developed and the reaction cycle time is reduced to almost one tenth of that without integration [65,66]. By using monolithic carbon discs, the heat transfer coefficient between the carbon bed and the fins can be increased about four times, and it is estimated that the cooling power can be enhanced by at least 90% higher than that of granular carbon [67].

### 2.1.2. Absorption cycle (gas–liquid)

Compared to adsorption technologies, the absorption heat pump technologies are further developed [76] and are more suitable for low-grade heat utilisation [77]. Water–lithium bromide ($H_2O$–LiBr) and ammonia–water ($NH_3$–$H_2O$) absorption cycles are the most commonly used cycles and have been applied commercially for years. Water–lithium bromide cycle has water as its absorbate, while ammonia–water cycle has ammonia as absorbate.

There are three fluid pipelines in an absorption cycle: one for rich absorbent solution, weak absorbent solution and pure refrigerant fluid each. The typical operating temperatures for the evaporator, generator, condenser and absorber were elucidated by Reay [78]. The working principles of the absorption cycle had been described in further details by Heppenstall [79]. Commercially available $H_2O$–LiBr systems have typically a COP of 0.7 for a single
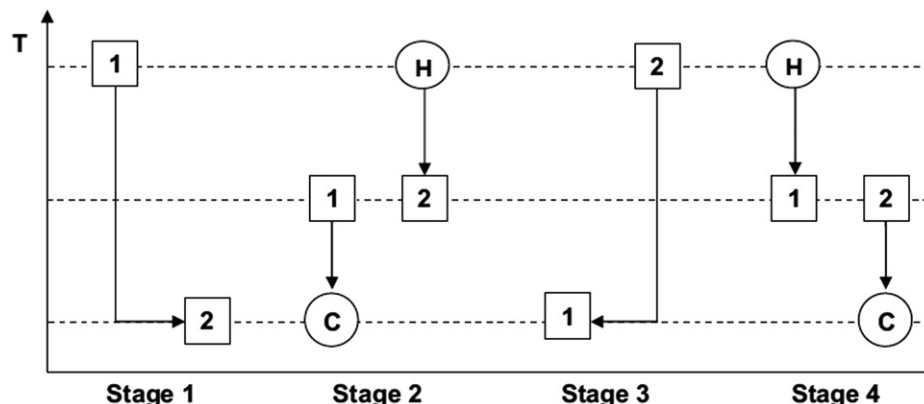


**Fig. 3.** Two-bed cycle, where H represents heat source, C represents heat sink and T represents temperature [45].
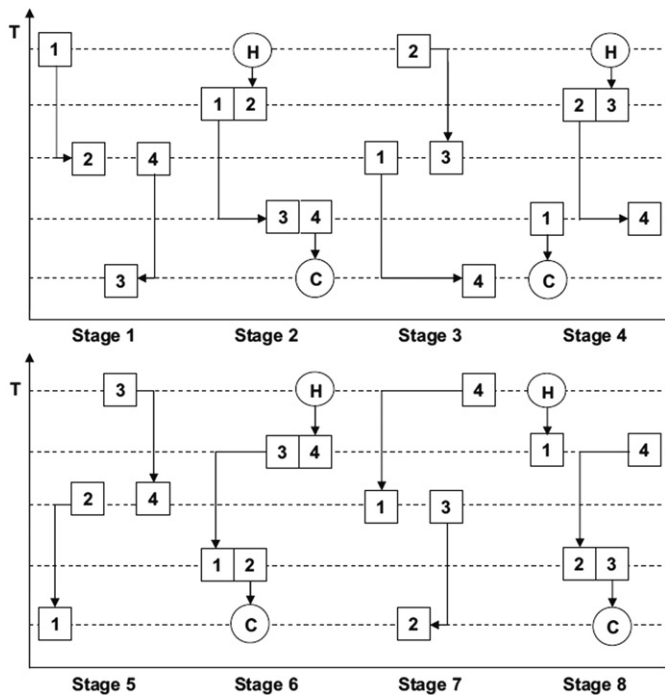
**Fig. 4.** Four-bed cycle, where H represents heat source, C represents heat sink and T represents temperature [45].

effect to a COP of 1.2 for a double effect [80]. A single stage $NH_3$–$H_2O$ system may have a COP as low as ~0.3 [81] to as high as ~0.6 [82]. The efficiency of the absorption system and the range of application temperature are determined by the number of stages (evaporator–absorber) and effects (generators or desorbers) [51]. Nevertheless, both $H_2O$–LiBr and $NH_3$–$H_2O$ cycles are associated with some problems. The former is more expensive, corrosive to some materials and suffers from possible vacuum loss due to the vacuum operating condition, while the latter is slightly toxic and requires a rectifier to efficiently remove residual water vapour from the ammonia vapour as the separation of ammonia from water–ammonia solution in the generator is imperfect.

Also, an absorption system that utilises salt, e.g. $H_2O$–LiBr system, is more susceptible to crystallisation which will hamper the efficiency of the system due to its saturation threshold. By conducting a review on the possible causes of crystallisation, Wang et al. [83] reached the following conclusions:

- Since absorption system operates under vacuum, air may leak into the system. Consequently, metal in the system becomes

corrosive and starts to generate non-condensable gas, particularly at higher-temperature operation. The presence of these gasses lowers the system capacity and COP. The absorbent solution becomes more and more concentrated. At one point, it turns super-saturated and triggers crystallisation [84];
- If the absorbate solution in the condenser is suddenly cooled down to a temperature lower than normal operating temperature, the temperature of the dilute absorbent solution leaving the absorber will drop as well. Accordingly, the temperature of the concentrated absorbent solution in the heat exchanger will reach a temperature which is lower than crystallisation point [85];
- Over-firing the generator will also result in super-saturation and crystallisation of the absorbent solution [85];
- If the machine is suddenly stopped due to power failure or other reason while operating at full load, the highly concentrated absorbent solution in the machine will inevitably cool down to ambient temperature and crystallise [85].

While chemical inhibitors can be used to prevent crystallisation, mechanical design can be adopted to lower the risk of crystallisation by enhancing heat and mass transfer performance, as briefly presented in Table 3.

The absorption cycle overcomes the drawbacks of the adsorption transportation system [50], as: (i) the energy transportation density of liquid is much higher than that of gas, consequently reducing the diameters of pipelines and the power consumption, and (ii) the absorption system operates continuously instead of intermittently. Fig. 6 illustrates an absorption model which utilises waste heat for district heating and cooling.

Recent work [105] on an ammonia–water absorption cycle using waste heat for district energy system concluded that the economic distance (which is a linear function of steel price) increases directly with the building heating price for both heating and cooling. As ammonia solution is transported at ambient temperature, the transportation will not experience any heat loss. The economic distance is independent of the low grade heat capacity because the requirement of larger pipes has counteracted the benefits of larger low grade heat capacity. A lot of initial investments involve pipe materials which is a function of its size. However, after a 3-year payback period, the profit becomes strongly correlated to the capacity of the system and this is no longer dependent on the nature of the heat sinks. Ammar et al. [105] estimated the annual profit and the $CO_2$ reduction for an absorption cycle applied for district heating/cooling by some energy intensive industries, as illustrated in Fig. 7(a) and (b) respectively.

Certain surfactant additives, such as n-octanol [106], can significantly improve the absorption rate by inducing the
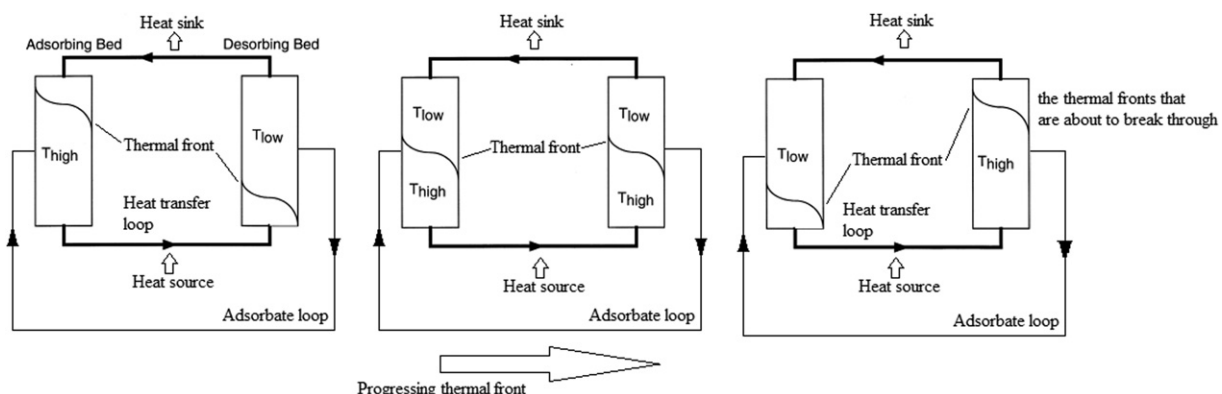


**Fig. 5.** The progression of temperature fronts through the adsorbent beds (adapted from [52]).

**Table 1**
Heat of adsorption for some typical adsorbent−adsorbate pairs (adapted from [54,55]).

| Adsorbent | Adsorbate | Heat of adsorption, kJ/kg |
|---|---|---|
| Silica gel | $CH_3OH$ | 1000−1500 |
|  | $H_2O$ | 2800 |
| Activated alumina | $H_2O$ | 3000 |
| Zeolite | $H_2O$ | 3300−4200 |
|  | $NH_3$ | 4000−6000 |
|  | $CO_2$ | 800−1000 |
|  | $CH_3OH$ | 2300−2600 |
| Charcoal/activated carbon | $C_2H_4$ | 1000−1200 |
|  | $NH_3$ | 2000−2700 |
|  | $H_2O$ | 2300−2600 |
|  | $CH_3OH$ | 1800−2000 |
|  | $C_2H_5OH$ | 1200−1400 |
|  | $CO_2$ | 680 |
|  | n-Butane | 406 |
|  | $H_2$ | 2800−3950 |
|  | $N_2$ | 418 |

Marangoni effect which reduces the surface tension at the liquid−vapour interface. This encourages convective flows that will enhance mass and heat transfer rates. Not only does the addition of surfactants result in a shorter absorption time, it can also lower the operating temperature of the absorber and the generator [107,108].

**Table 2**
A summary of the methods for enhancing heat transfer in reactor beds for chemical heat pumps [68].

| Heat transfer promoter | Preparation technique | Reaction couple |
|---|---|---|
| Expanded Graphite (EG) | Simple mixing | $CaCl_2/NH_3$ [69] |
|  | Impregnation of aqueous solution of salt using EG, dehydration and calcination | $CaCl_2/CH_3OH$ [56]; $CaCl_2/CH_3NH_2$ [57] |
|  | Impregnation of aqueous solution of salt using EG, dehydration, acidification and calcination | $CaCl_2/NH_3$ [70] |
|  | Impregnation of aqueous solution of salt into compressed EG, dehydration and calcination | $CaCl_2/CH_3NH_2$ [58]; $MnCl_2/NH_3$ [58,59]; $CaCl_2/NH_3$ [59]; $BaCl_2/NH_3$ [59] |
|  | Mixing activated carbon with compressed EG using resin as a binder | Activated Carbon/ $CO_2$ [62] |
| Carbon fibre | Impregnation of aqueous solution of salt into fibre and dehydration | $CoCl_2/NH_3$ [71] |
|  | Insertion of carbon fibre brush into bed | $MgO/H_2O$ [64] |
|  | Formation of an intercalation compound | $MnCl_2/HN_3$ [72] |
| Metal foam (Cu, Ni) | Impregnation of a suspension salt, compression and calcination | $Zeolite/H_2O$ [73]; Activated carbon/ $CH_3OH$ [73] |
| Resin (polyanilin) | Coating particles with resin network | $Zeolite/H_2O$ [74] |
| Aluminium hydroxide | Mixing, compression and calcination | $Zeolite/H_2O$ [75] |
|  | Insertion of fins into bed | $CaO/H_2O$ [63] |
| Metal fin or tube | Integration of reactant with heat exchanger by coating fin tubes with an adsorbent layer | Silica gel/$H_2O$ [65]; $Zeolite/H_2O$ [66] |
|  | Forming monolithic carbon discs and insertion into aluminium fins | Activated carbon/$NH_3$ [67] |

**Table 3**
Techniques to inhibit crystallisation in a $H_2O$−LiBr absorption system.

|  | Resources |
|---|---|
| *I. Using chemical inhibitors* |  |
| Lithium chromate ($LiCrO_4$) | [86] |
| Ethylene glycol ($C_2H_6O_2$) at a weight ratio of lithium bromide (LiBr) to ethylene glycol of 4.5:1. Since a traceable amount of ethylene glycol could possibly exist in the vaporised refrigerant, rectification is needed. | [87−89] |
| 1,3-Propanediol (HO$(CH_2)_3$OH) which will tolerate for 8% higher crystallisation limit. | [90,91] |
| Lithium nitrate ($LiNO_3$) works as a crystallisation inhibitor and corrosion inhibitor. Lithium iodide (LiI) is also selected as a crystallisation inhibitor, and lithium chloride (LiCl) serves as a vapour pressure suppression agent. The system with lithium halides had been patented in Japan. | [92−94] |
| 27 Crystallisation inhibitors (at concentrations of 250−1500 ppm) are identified; LiBr solutions cool down at a rate of 20 °C h$^{-1}$. | [95,96] |
| *II. Adopting mechanical design* |  |
| Vertical falling-film heat exchangers are used as absorbers. | [87,94] |
| A vertical vibrating screen is used to enhance the heat and mass transfer of working fluid in the absorber. | [97] |
| A spray absorber utilises pressure atomisation of working fluid to increase the heat and mass transfer rates by increasing the area exposed to the brine solution. | [98,99] |
| Absorption chiller unit in a climate-controlled environment with rotating heat exchangers as absorbers and generators. The centripetal force forms thin films in order to improve heat and mass transfer. | [100,101] |
| Mechanical compression devices such as axial-flow fans to lift the pressure of the absorber to reduce crystallisation. | [102] |
| Crystallisation is more prone to occur in a strong solution entering the absorber. When crystallisation occurs, strong solution entering the absorber would be forced back up to the generator, where the hot, highly concentrated solution will bypass or overflow into the absorber through the J-tube to immediately increase the temperature of the low-concentrated solution. | [103] |

Accordingly, work output and the respective COP will also increase, as shown in Table 4.

Various alcohols with higher molecular weight are known to be good additives for $H_2O$−LiBr absorption cycles operating in moderate temperature range (293−333 K), and among all, n-octanol is the most prominent one [106]. Kang et al. [109] did some preliminary studies on the types of surfactants that can decrease surface tension of the $NH_3$−$H_2O$ interface. However, there is very little literature about improved absorption capacity or energy efficiency for the application of Marangoni-induced effect on absorption heat pumps.

Nanofluids can not only enhance mass diffusivity [110] and radiative heat transfer characteristics [111,112], but also potentially improve the performance of heat pump absorption cycles. The dispersion stability of particles within the fluid can be improved using nanoparticles without greatly affecting other physical properties, such as viscosity and density. Lee et al. [113] found that the addition of carbon nanotubes in an absorption cycle (at 0.02 vol%) can result in an increase of 17% of the heat transfer rate and 16% of the absorption rate if compared to those without nanoparticles, while 0.02 vol% of $Al_2O_3$ can result in an increase of 29% of the heat transfer rate and 18% of the absorption rate respectively.

The major problem with nanotechnology [114] is that although nanoparticles disperse fairly easily, they agglomerate easily as well. Once nanoparticles agglomerate, their effective diameter and settling rates increase dramatically. Two types of nanoparticle dispersion methods are generally used:
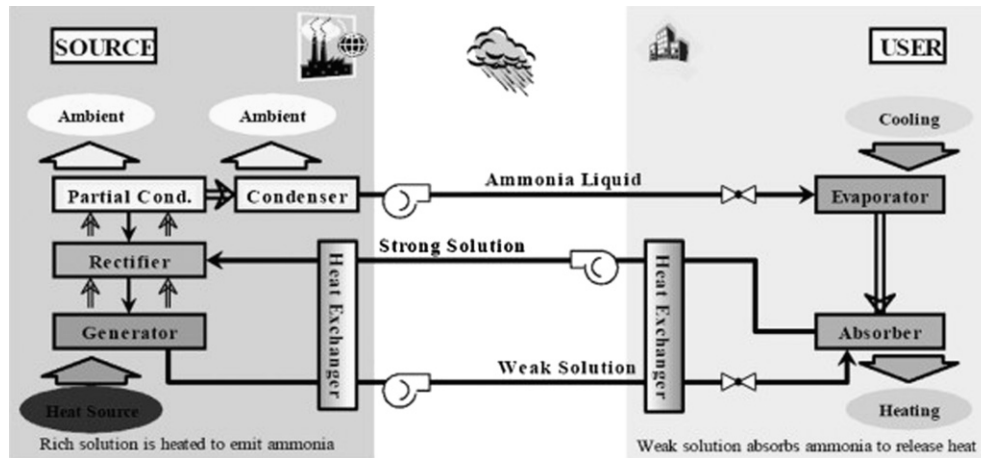
**Fig. 6.** Transportation of low grade heat by absorption process [104].

- Physical dispersion including high-shear mixing and ultra-sonication; however long term stability may not be obtained without chemical stabilisation.
- Chemical stabilisation is used to overcome van der Waals forces between particles that lead to agglomeration. Chemical stabilisation methods that have been used to date are electrostatic and steric dispersion, as well as surface modification through the use of self-assembled monolayers [115,116]. These methods offer increased dispersion stability over the physical methods.

### 2.1.3. Summary

The performance improvement of chemical heat pumps can be achieved by various approaches applicable to different cycles:

(i) Adsorption cycles:
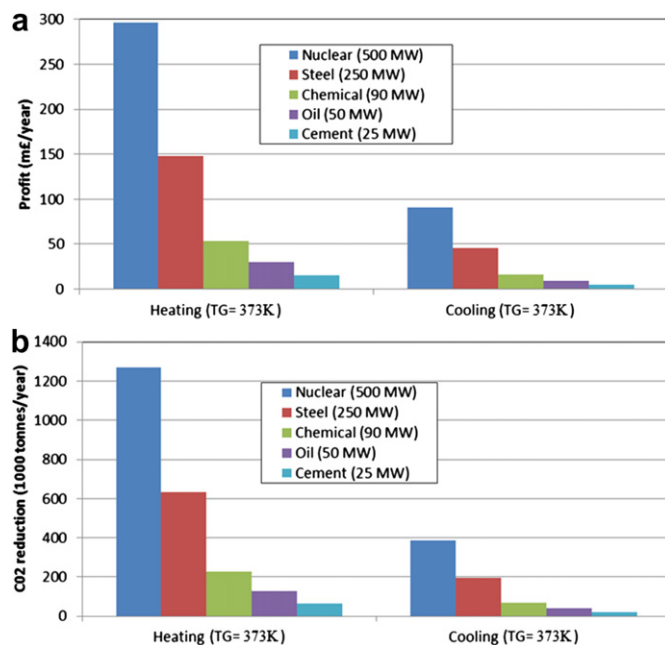- Increasing multiple beds cycle or thermal wave process can reduce the intermittency of heat transport process;



**Fig. 7.** (a) Profit related waste heat capacity, and (b) $CO_2$ reduction related waste heat capacity [105], where TG is the temperature of the generator.

- Adopting heat transfer improvement techniques, which are defined into three categories:
  - ○ preparation of a composite adsorbent with heat transfer promoter;
  - ○ addition of metals or carbon fibres into a bed; and
  - ○ integration of a reactant into a heat exchanger.

(ii) Absorption cycles:
- Using Marangoni surfactant additives, although not many compounds have been identified yet. Also, the effect of Marangoni additives on the absorption cycle has not been fully explored in the technical, practical and economic aspects.

### 2.2. Thermodynamic cycles and efficiency improvement

Various thermodynamic cycles such as the organic Rankine cycle (ORC), the supercritical Rankine cycle (SRC) and the trilateral cycle (TLC) have been studied for the conversion of low-grade heat sources into electricity. This section focuses on the research work done so far by other investigators on the ORC, SRC and TLC. The expander component, which is shared by these thermodynamic cycles, and zeotropic mixtures as working fluid are also discussed.

### 2.2.1. Organic Rankine cycles (ORCs)

The ORC, occasionally referred to as the subcritical ORC, is currently used in various industrial low grade heat applications, such as binary geothermal power plants, solar thermal power systems, solar ORC-RO (reverse osmosis) desalination systems, Duplex-Rankine systems, ocean thermal energy conversion

**Table 4**
Simulated results of absorption cycle for working fluid with and without surfactants (adapted from [106]) where '+' represents heat input and '−' represents heat output.

| Section | LiBr (60–65% by mass) | | LiBr, sodium formate & n-octanol[a] | |
|---|---|---|---|---|
| | Power | Temperature | Power | Temperature |
| Evaporator | +1580 kW | 279 K | +2124 kW | 279 K |
| Absorber | −1730 kW | 313 K | −2321 kW | 288 K |
| Generator | +1850 kW | 375 K | +2259 kW | 335 K |
| Condenser | −1636 kW | 319 K | −2141 kW | 319 K |
| Absorption rate, kg/h | 2346 | | 3168 | |
| COP | 0.85 | | 0.94 | |

[a] 40.54%−45% of the solution is lithium bromide and sodium formate with concentration ratio of 2:1 respectively, while n-octanol is at 1000 ppm.

systems, waste heat recovery applications and biomass power plants, as described in detail by Tchanche et al. [117]. There is even hybrid application in the form of ORC-absorption technology but only at research stage [118–120]. The temperature–entropy diagram of ORCs can be either bell-shaped or overhanging [121]. To give an example, the configuration of an ORC and its temperature–entropy chart are illustrated in Fig. 8.

Its working principles are similar to a Rankine cycle. The working fluid is pumped from low to high pressure with only little energy input (1 → 2). A regenerator can be added (optional) to improve the efficiency of the ORC, where the higher temperature fluid leaving the expander (6 → 7 → 8) can be used to preheat the lower temperature fluid (2 → 3 → 4) before it enters an evaporator. After entering the evaporator, the liquid is heated at constant pressure by an external heat source and becomes a dry saturated vapour (4 → 5). The dry saturated vapour expands in the expander and generates power (5 → 6). This decreases the temperature and pressure of the vapour, which is then condensed at a constant temperature in a condenser to become saturated (8 → 1) before it is pumped to the evaporator.

While Rankine cycles usually operate at temperatures above 673 K, the ORC works effectively at lower temperatures, typically between 373 K and 673 K because in an ORC cycle:

- evaporation takes place at lower pressure and temperature;
- expansion ends in the vapour region, hence superheating is not required; and
- the smaller temperature difference between evaporation and condensation leads to a much smaller pressure drop ratio which allows the use of single stage turbines.

The working fluid of an ORC determines its economics and operating performance, as outlined by Tchanche et al. [123], who also proposed some potential working fluids and identified their desirable characteristics. In designing an ORC, both temperatures at the condenser and the evaporator exhaust should be kept as low as possible when using high molecular weight organic fluids [124–126]. An increase in evaporating temperature will not only increase the under-expansion losses in the expander, which reduces its efficiency, but also decrease the heat recovery efficiency as the heat source cools down to a higher temperature.

Schuster et al. [127] estimated that the specific investment cost for an ORC was €3755/kW$_{el}$. However the figure presented was for the application of energy recovery in biogas digestion plants which produced an additional 35 kW of electrical power, hence the investment cost as such may not be representative for larger

practical application, that can have capacities ranging from 125 kW to 6.5 MW [117]. Quoilin et al. [128] showed that the cost of an ORC system decreases with increasing evaporating temperature, and that the expander component contributes significantly to the overall cost. The influence of the evaporating temperature on the cost is significant [128] because increasing evaporating temperature increases the vapour density which reduces the pressure drops in the heat exchangers and the required swept volume of the expander. Using the equations listed in Table 5, the total investment cost of an ORC can be estimated (however the reference does not clearly indicate how the formulae were derived). A careful economic analysis taking into account all components in an ORC (which is however not within the scope of this paper) deserves a detailed discussion.

The recent work by Quoilin et al. [128] on six different kinds of working fluids, with evaporating temperature between 367 K and 416 K, reported that the efficiency of an ORC is generally between 5 and 9% (net electrical output over the actual amount of low grade heat transferred to the evaporator) while the overall efficiency is between 2 and 5% (net electrical output over the amount of low grade heat available, but which may not be completely transferred to the evaporator).

### 2.2.2. Supercritical Rankine cycles (SRCs)

The configuration of an SRC and its temperature–entropy chart are illustrated in Fig. 9. The working fluid can be $CO_2$, $H_2O$ or organic (hydrocarbons) which is heated directly from a liquid state into a supercritical state bypassing the two-phase region to allow a better thermal match with the heat source resulting in less exergy destruction [129] and negating the need to use phase separation equipment. $H_2O$ based SRC is not elaborated in further detail in this paper since the minimum supercritical temperature required is 647.1 K which is beyond the range of the low grade heat temperature (<523 K) defined earlier in the paper, whereas the minimum supercritical temperatures for $CO_2$ (304.1 K) and hydrocarbons, both are less than 523 K. SRC is also known as a transcritical Rankine cycle [122]. SRCs for low grade heat applications [129–132] have not been as widely studied and researched as its higher temperature counterparts. Its working principles are similar to that of the ORCs. The working fluid is initially pumped from low to high pressure with only little energy input (1 → 2). The high pressure fluid then enters a heat recovery vapour generator and forms a supercritical fluid under constant pressure (2 → 3). The supercritical fluid expands in the expander and generates power (3 → 4). This decreases the temperature and pressure of the supercritical fluid. The supercritical fluid then enters a condenser
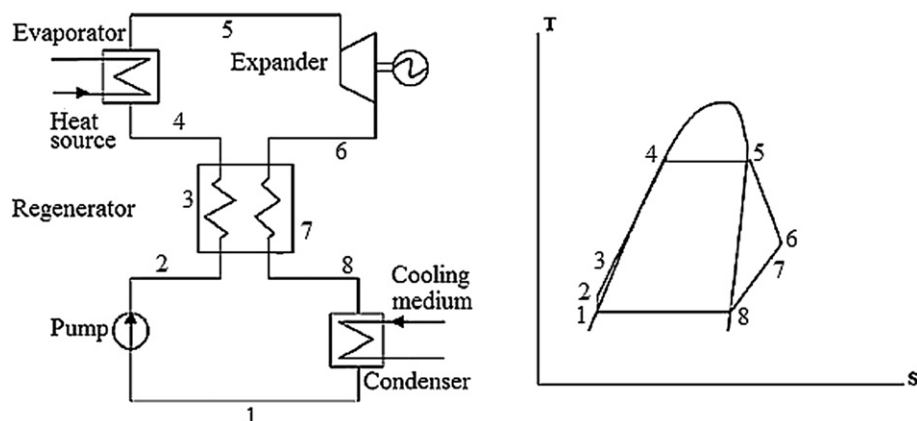


**Fig. 8.** Organic Rankine cycle system for low grade heat recovery and its T–S (temperature–entropy) chart [122].

**Table 5**
Component costs [128].

| Component | Dependent variable | Cost (€) |
|---|---|---|
| Expander | Volumetric flow rate, $Q_v$ (m³ s⁻¹) | $1.5 \times (225 + 170 \times Q_v)$ |
| Heat exchangers | Heat exchange area, $A$ (m²) | $190 + (310 \times A)$ |
| Working fluid pump | Electrical power, $W$ (W) | $900 \times (W_{pp}/100)^{0.25}$ |
| Heat transfer fluid pump | Electrical power, $W$ (W) | $500 \times (W_{pp}/100)^{0.25}$ |
| Liquid receiver | Volume, $V$ (m³) | $31.5 + 16 \times V$ |
| Piping | Pipe diameter, $d_{pipe}$ (mm) | $(0.897 + 0.21 \times d_{pipe}) \times L_{pipe}$ |
| Working fluid | Mass, $M$ (kg) | $20 \times M$ |
| Miscellaneous hardware | – | 300 |
| Control system | – | 500 |
| Labour | Total component costs, TCC (€) | $0.3 \times TCC$ |

$L_{pipe}$ is the length of pipe in m.

where it is cooled down to condensing temperature and forms a saturated liquid, which is then pumped to the heat recovery vapour generator (4 → 1).

Similar to ORCs, the choice of working fluids plays a key role for the performance of an SRC. By conducting a carbon dioxide ($CO_2$) based SRC study, a few researchers [134–136] reported that the power generation efficiency of the cycle ranges between 8.0% and 11.4%. Furthermore, Chen et al. [130] did a comparative study between a $CO_2$-based SRC and an R123-based ORC, concluding that under the same thermodynamic mean heat rejection temperature,

- the $CO_2$-based SRC gives a slightly higher power output than the R123-based ORC;
- the $CO_2$-based SRC operates at pressures as high as 16 MPa; and
- the $CO_2$-based SRC does not condense $CO_2$ due to its low condensation temperature.

Besides $CO_2$, fluids such as hydrocarbons [137] have also been studied as the working fluids of SRCs, and the results showed that the thermal efficiency of SRCs can be improved by 10–20%, compared to the same working fluids studied by Karellas and Schuster [129] in ORCs. Chen et al. [130] have commented that although thermal efficiency for SRCs can be lower than ORCs, SRCs are actually capable of recovering more heat than ORCs since SRCs have a larger heat source temperature drop than that of ORCs. Recent work reported by Chen et al. [122] claimed that an SRC can achieve 10.8–13.4% thermal efficiency with a cycle temperature between 393 K and 473 K, compared to an ORC which has 9.7–10.1% thermal efficiency (the thermal efficiency for an SRC is 10–30% higher than that of an ORC); meanwhile the SRC exergy

efficiency will reach 38.6% while that of an ORC will be 24.1% when heating and condensation processes are taken into account.

### 2.2.3. Trilateral cycles (TLCs)

The TLC, also known as the trilateral flash cycle (TFC), is a thermodynamic cycle where expansion starts from a saturated liquid state rather than a vapour phase. Based on the work done by Smith [138], Badr et al. [139] suggested that the TLC can be referred to as the trilateral wet vapour cycle. The configuration of a TLC and its temperature–entropy chart are illustrated in Fig. 10.

Similar to the ORCs and SRCs, the working fluid of a TLC is pumped from low to high pressure with only little energy input (1 → 2). Under constant pressure, the high pressure liquid becomes saturated (2 → 3) and then expands in the expander to generate power (3 → 4). This decreases the temperature and pressure of the liquid which produces a fraction of gas. The gas–liquid working fluid is then condensed completely and forms a saturated liquid in a condenser before it is pumped to the heater (4 → 1 → 2 → 3).

By avoiding the boiling phase, the heat transfer from a heat source to a working fluid can be achieved with good temperature match where less temperature difference between heat source and the evaporating temperature of the working fluid is desirable. Irreversibility is therefore minimised. The study of Steidel et al. [140] claimed that the potential power recovery of a TLC can be 14–85% more than that of an ORC, while Löffler [141] estimated that TLCs can have efficiencies which are 50–100% higher than ORCs. Model calculations presented by Zamfirescu and Dincer [142] concluded that the exergy efficiency for a TLC which uses ammonia–water mixtures as working fluids is 2–3 times higher than that of an ORC which uses various hydrocarbons as working fluids.

Using water as a working fluid, Fischer [133] found that slightly subcritical or supercritical pressures are required for optimal operation which could result in a 14–20% higher exergy efficiency of power production (the ratio of the net power output to the incoming exergy flow of the heat carrier) than that of an ORC. The total exergy efficiency (ratio of all outgoing exergy flows to all incoming exergy flows) is slightly higher for the TLC than that of the ORC, between 1% and 9%. The application of a TLC with water as working fluid is mainly recommended by Fischer [133] for higher values of the minimum working fluid temperature or higher inlet temperature of the cooling agent. No work has yet been reported on working fluids with high vapour pressures, e.g. hydrocarbons [133].

### 2.2.4. Expander

The expander constitutes a large part of the total investment cost in the application of a thermodynamic cycle; hence improved efficiency will drastically reduce cost [128]. Two types of expanders have been actively researched, namely volumetric expanders and
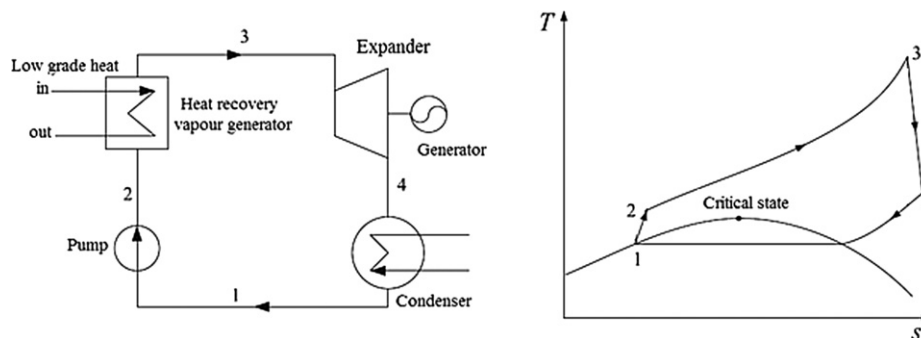
**Fig. 9.** Supercritical Rankine cycle system for low grade heat recovery and its $T$–$S$ (temperature–entropy) chart (adapted from [133]).
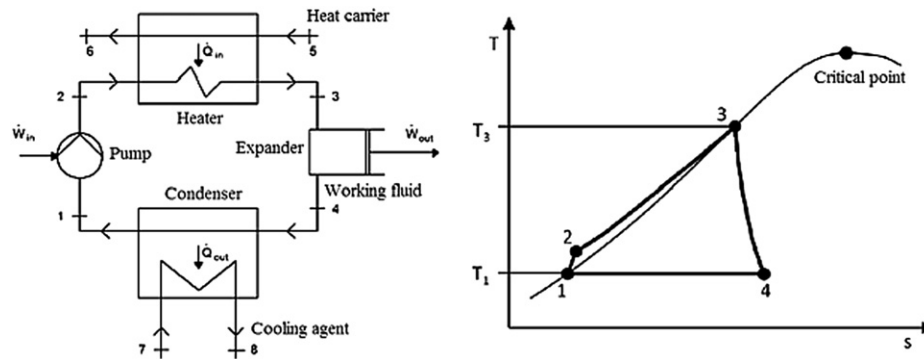
**Fig. 10.** Trilateral Rankine cycle system for low grade heat recovery and its T–S (temperature–entropy) chart (adapted from [133]).

screw expanders. The former generally has less moving parts, is more reliable with wider output power range and broadly available with good isentropic effectiveness [143] ranging from 48% to 68% [144–147] which is suitable for small scale power generation. The latter provides an even more promising solution as they are better adapted to larger capacities and show the advantage of accepting a high liquid fraction at the inlet, allowing for the design of wet cycles [148].

### 2.2.5. Zeotropic mixtures

A review of the literature shows that research studies on SRCs and ORCs have merely focused on pure fluids [137,149,150]. However, the application of pure fluids in ORCs is limited due to its constant evaporating temperature hence there may be a mismatch between evaporating temperature of the working fluid and the available low grade heat source. Although SRCs which use pure fluids as working fluids can overcome the pinch point limitations of ORCs during the heating process, the condensation process remains isothermal. A zeotropic mixture as working fluid is desirable and of research interest because it can have a variable vapour–liquid equilibrium state. It is worth noting that a zeotropic mixture normally shows the same thermodynamic properties as the pure fluids through different component mass fractions [151]. Substituting pure working fluids for zeotropic mixtures can result in a higher efficiency due to lower exergy destruction during boiling and condensation [122,133]. The use of a zeotropic mixture can minimise the irreversibility of the thermodynamic cycles because the zeotropic mixture generally shows variable temperatures during the phase change process. This reduces the mismatch of temperature profiles between working fluid and heat source.

Chen et al. [122] compared the performance of an R134a-based conventional ORC with a zeotropic mixture-based SRC under the same temperature limits and their findings are shown in Table 6. It is claimed that the zeotropic mixture-based SRC is more efficient compared to an ORC. Heberle et al. [152] stated that for heat source temperatures below 393 K, the efficiency of the cycle (based on the second law of thermodynamics) increases about 4.3–15% relative to

the most pure components. In total, 28 working fluids which are suitable as zeotropic mixtures have been identified and proposed by Chen et al. [122]. The performance of various thermodynamic cycles are summarised from a range of literature reviews in Table 7. It is important to note that there are already commercial applications of ORCs [153] and SRCs [154], however the TLC is still in the developmental stage [142] and the authors are unaware of any commercial applications of TLCs.

### 2.2.6. Summary

A few thermodynamic cycles capable of converting low grade heat into electricity were reviewed:

(i) Organic Rankine cycles (ORCs): A lot of research has looked into various hydrocarbons and attempted to identify the optimum working fluid.
(ii) Supercritical Rankine cycles (SRCs):
   - the working fluid is supercritical which bypasses two-phase region, hence enabling better thermal match with the heat source;
   - there is less exergy destruction because no phase separation equipment is required;
   - research is needed on the appropriate working fluids (hydrocarbons); and
   - 10–30% increase in thermal efficiency relative to the ORC is possible.
(iii) Trilateral cycles (TLCs): These cycles have efficiencies which are 50–100% higher than those of ORCs, although very little research has been done so far.

The expander component of the cycles constitutes a large part of the total investment cost in the application of a thermodynamic cycle; hence an improved efficiency will drastically reduce cost. Two types of expanders have been actively researched, namely volumetric expanders and screw expanders. Research into using zeotropic mixture as a working fluid is still at its infancy. This mixture has a variable vapour–liquid equilibrium state, hence allowing for a better match with the heat source.

### 2.3. Thermal energy storage

Thermal energy storage is important since its application may improve the performance of energy systems. There has been active research in the application of thermal energy storage in CHP [158–161], tri-generation [162,163], and district energy systems, i.e. heating and cooling [164–166], space heating [167], etc. Further enhancement of the total energy system performance can be achieved by improving the performance of the energy storage media.

**Table 6**
Comparison of the efficiency between a pure fluid (R134a) ORC and a zeotropic SRC [122].

| Working fluid and thermodynamic cycle | R134a, ORC | Zeotropic mixtures (R134a and R32), SRC |
|---|---|---|
| Exergy efficiency of the cycle (%) | 43.8 | 53.3 |
| Exergy efficiency of condensation (%) | 66.6 | 81.6 |
| Exergy efficiency of heating (%) | 82.6 | 88.7 |
| Total exergy efficiency of the system (%) | 24.1 | 38.6 |

Zeotropic mixture of R32 and R134a (0.3/0.7, mass fraction).

**Table 7**
Comparison of typical performance of low grade heat technologies for power generation, modified from [155].

| Sources | Technology | $\eta_{th}$ | $\eta_{ex}$ | Heat source | Relative cost |
|---|---|---|---|---|---|
| [121,156] | ORC | 8–20% | 25–45% | 373–573 K | Intermediate |
| [122,156,157] | SRC (supercritical organic working fluid) | 10–25% | 30–50% | 373–573 K | High |
| [133] | TLC | – | 28.5–58% | 423–623 K | – |

$\eta_{ex}$: exergy efficiency, $\eta_{th}$: thermal efficiency.

This section discusses two forms of thermal energy storage: sensible thermal energy storage and latent thermal energy storage with phase change materials (PCMs), and the media used in each storage system.

### 2.3.1. Sensible thermal energy storage

When energy is stored or extracted by heating or cooling a medium without undergoing phase change, it is called sensible thermal energy storage. Sensible thermal energy storage systems are simple in design, but larger in size and cannot store or deliver energy at a constant temperature. The typical sensible thermal energy storage media can be liquids, e.g. hot water, organic liquids, molten salts and liquid metals, or solids, e.g. metals, minerals and ceramics.

The selection of the medium depends on a few factors [168], including:

- the temperature level of the application;
- the value of the heat capacity, $\rho.C_p$ where $\rho$ is the density of the material in kg m$^{-3}$ and $C_p$ is the specific heat capacity in kJ kg$^{-1}$ K$^{-1}$;
- the volume required due to the limitations in transport and/or habitat applications (denser materials generally have a smaller volume but larger energy capacity per unit volume); and
- the cost.

Table 8 summarises the advantages and disadvantages of using water and solid media as sensible thermal energy storage systems.

A common scenario associated with sensible thermal energy storage media is thermal stratification, which is also known as temperature-ordered stratification. In water, thermal stratification manifests itself in the form of different density layers. This is due to the buoyancy difference between the less dense but hotter water at

the top and the denser but colder water at the bottom. Fig. 11 illustrates a thermally stratified tank. In principle, perfect stratification (or density layers that do not inter-mix) is not achievable [169] as: (i) water entering the tank will cause a certain amount of agitation and mixing; (ii) diffusion due to temperature differences will take place, and (iii) natural convection due to heat loss at the surface of the storage tank, all of which will destroy the perfect stratification.

The storage tanks should be suitably insulated with glass wool, mineral wool or polyurethane to avoid heat loss that can destroy temperature layers. The insulation used is generally thick and ranges from 10 to 20 cm contributing to a significant part of the total cost. Besides, other possibilities to enhance the performance of sensible thermal energy storage systems are also considered, such as:

- employing multiple storage tanks at different temperatures, with the liquid in different tanks remaining at different temperatures even when the liquid in each tank is completely mixed, due to the physical separation between tanks;
- use of rock beds, since hot air is brought in contact with different parts of the rock bed in the path of its flow and these parts of the rock bed, heated to different temperatures, cannot mix;
- installation of an underground tank using the earth surrounding the tank as insulation. However it may take as much as one year for the earth around a large storage tank to reach a thermal steady state;
- water storage at a temperature which is a little above 373 K by using pressurised tanks.
- employing large scale storage which exists in nature, such as using underground aquifers which already contain water. Hot water is pumped into aquifers and stored, displacing the

**Table 8**
Summary of sensible heat storage systems (adapted from [169]).

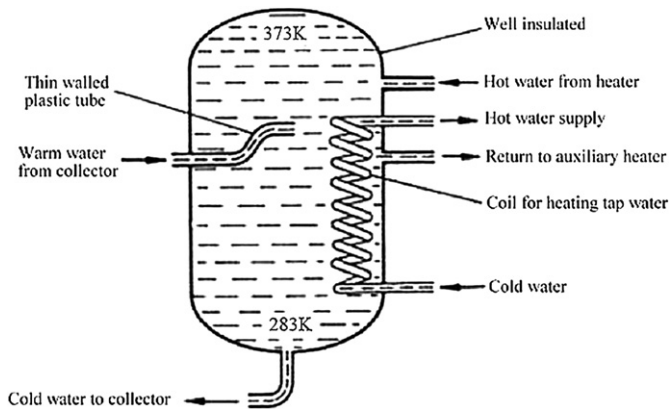| Sources | Advantages | Disadvantages |
|---|---|---|
| Water | • Simplicity;<br>• Inexpensive, easy to handle, nontoxic, non-combustible and abundant;<br>• High specific heat and high density;<br>• Heat exchangers may be avoided if water medium is used for transport;<br>• Natural convection flows can be utilised when pumping energy is scarce;<br>• Simultaneous charging and discharging;<br>• Adjustment and control is variable and flexible. | • Larger volume and weight relative to latent heat storage;<br>• Adjustment and control is variable and flexible resulting in pressure build up or volume expansion, destroying tanks;<br>• Can be highly corrosive;<br>• Working temperatures are limited to less than 373 K;<br>• Can be difficult to stratify. |
| Solid storage media | • Below 373 K, using water as heat transfer fluid, it is simple in design and relatively inexpensive;<br>• Rock/pebble-bed storages can also be used for temperatures of up to 1273 K, and still be inexpensive with high specific heat;<br>• Act as heat transfer surface and<br>• Medium<br>• Large heat transfer area<br>• Non-toxic and non-flammable; | • Cost rises sharply for temperatures above 373 K, as storage tanks must be able to contain water at its vapour pressure;<br>• Organic oils, molten salts and liquid metals use are limited because of their handling, containment, storage capacities and cost;<br>• Larger amounts of solids are needed than using water, due to lower storing capacity than water. |

**Fig. 11.** An example of a thermally stratified water tank (adapted from [169]).

existing cold ground water. The investment cost is low as it only requires a series of openings for water injection and removal (see Fig. 12).

A solar pond is an artificial pool of saltwater that collects solar thermal energy. In practice, it is a form of thermal stratification that can be influenced by salinity gradient. Most of the research efforts are presently concentrated on the non-convecting salt gradient solar pond which has a density gradient created by using saltwater (or sea water) [170]. Sodium chloride (NaCl) and magnesium chloride ($MgCl_2$) are most commonly used salts. The salt concentration in a solar pond increases with depth.

Amongst five alternative heat rejection methods from power plants studied by Leffler et al. [171], four of them reutilised waste heat. Performance of solar ponds could further be supplemented by (i) storing waste heat rejected by fossil-fuelled or nuclear power

plants, or (ii) reusing exhaust gas (393–403 K) emitted from a typical pulverised coal power plant [172] for potential use such as district heating. The total quantity of heat received by such a solar pond will be a function of the size of the power plant and the total surface area of the solar pond (at a solar irradiance of ~1400 W/$m^2$).

There are 3 distinct layers, namely the top layer or Upper Convective Zone (UCZ) which has a low salt content; the intermediate insulating layer with a salt gradient or Non Convective Zone (NCZ) which establishes a density gradient that prevents heat exchange by natural convection; and the bottom layer or Lower Convective Zone (LCZ) which has a high salt content. The extraction of the thermal energy stored in the lower layers of the pond can easily be accomplished without disturbing the upper layers. The heat extraction is shown in Figs. 13 and 14.

Ideally, the solar pond should be translucent to allow as much sunlight as possible to travel through and reach the bottom, thus the bottom of the pond could have high radiation absorption. When solar energy is absorbed in the water, the temperature of the water increases, causing thermal expansion that reduces its density. The salinity gradient forms a density gradient that increases with depth which counteracts the temperature gradient and prevents heat in the lower layers from moving upwards by convection. This means that the temperature at the bottom of the pond can rise to over 363 K while the temperature at the surface of the pond is usually around 303 K. The maintenance of solar ponds includes constantly replenishing the evaporated surface water and removing the accumulating salt crystals which can be a valuable by-product to increase their economic viability.

Leblanc et al. [173] claimed that the energy efficiency of a solar pond can be increased by 55% with a heat supply ranging between 323 K and 363 K. This is done by using a novel method to extract heat from a solar pond by drawing heat from the gradient layer (NCZ). Maintaining a stable density gradient at NCZ with a sufficient depth is the key for successful application. The LCZ, NCZ and UCZ boundaries can be maintained by diluting the UCZ and adding salt to the LCZ. The levelised cost of energy (LCOE), which is 'the average price consumers would have to pay to exactly repay the investor for capital and fuel costs with a rate of return equal to the discount rate' [174], ranges from US $6.60/GJ for a 1-ha pond to US $1.30/GJ per 100-ha at 200 W $m^{-2}$ of solar radiation. The LCOE for heat delivery compared to heating cost of natural gas and coal was studied by Leblanc et al. [173]. The loss of salt from the LCZ and the NCZ can be compensated by adding solid salt or high concentration brine to these layers. A further analysis is required to evaluate if the
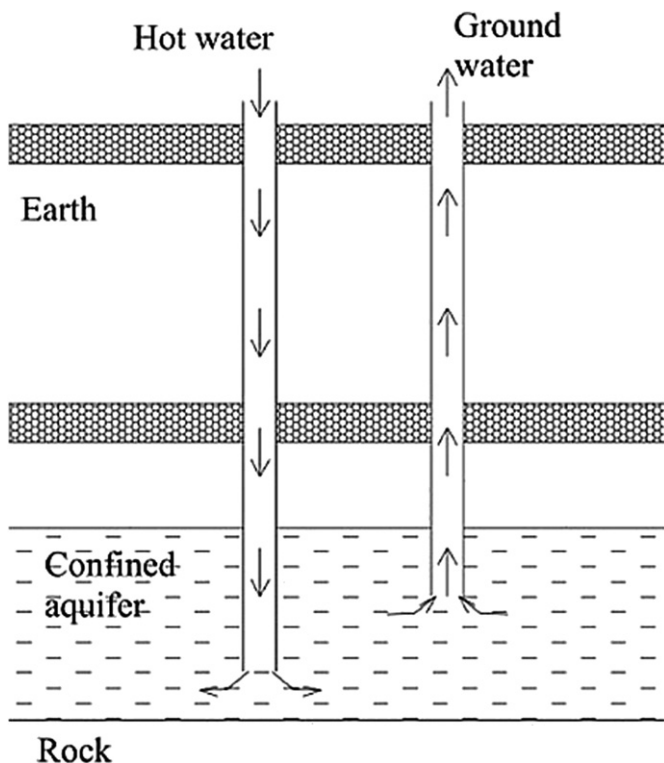


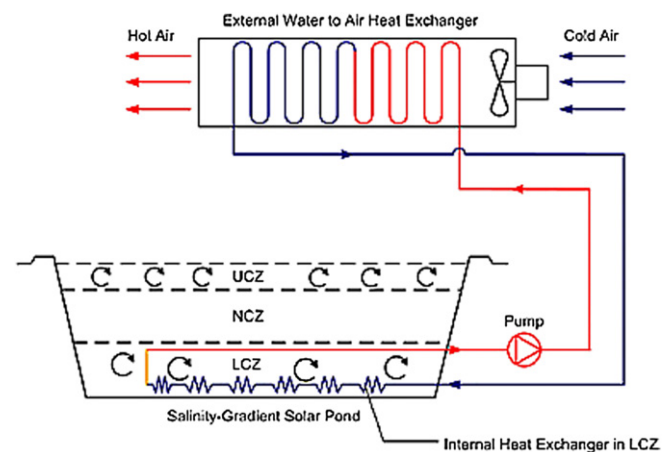**Fig. 12.** Thermal storage using natural aquifer [169].



**Fig. 13.** Conventional method of heat extraction using an internal heat exchanger [173].
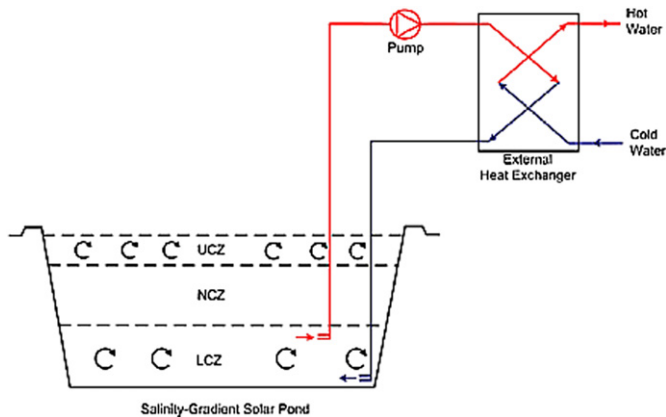
**Fig. 14.** Conventional method of heat extraction using an external heat exchanger [173].

economic gains from increased thermal efficiency can recoup the additional capital and operating costs of the gradient-layer heat extraction system.

The consideration and application of solar ponds for power generation is not elaborated in this paper due to its sheer size, relative to base load power plant. For more information, the reader is referred to Akbarzadeh et al. [175].

### 2.3.2. Latent thermal energy storage with phase change materials (PCMs)

Latent thermal energy storage with phase change materials (PCMs) is attractive as it provides high energy density storage due to phase change of a material by freezing/melting. The study of PCMs was pioneered by Telkes and Raymond [176]. PCMs can be organic and inorganic which have been presented and summarised by many authors [177–180]. Relative to sensible energy storage systems, latent thermal energy storage with PCMs requires a smaller weight and volume of material for a given amount of energy, and has the capacity to store heat of fusion at a constant or nearly constant temperature. Table 9 summarises the required properties of PCMs, while Table 10 summarises their respective advantages and disadvantages.

Performance of PCMs can be enhanced by incorporating them into heat exchangers or inserting heat pipes into PCM containers. The former has higher energy storage density compared to other PCM storage (encapsulation) but smaller heat transfer area. The heat transfer fluid (HTF) may flow along inner cylinder [166,185] or

**Table 9**
Required properties of PCMs [177,181].

| Characteristics | Properties |
|---|---|
| Thermal | • Phase change temperature in suitable operating range<br>• High latent heat per unit mass<br>• High specific heat |
| Physical | • High density<br>• Low density variation during phase change<br>• Little or no super-cooling<br>• Low vapour pressure of melt |
| Chemical | • Chemical stability<br>• No chemical decomposition<br>• Compatibility with container materials<br>• Non-poisonous, non-flammable and non-explosive |
| Economic | • Available in large quantities<br>• Inexpensive |

**Table 10**
Typical advantages and disadvantages of organic and inorganic PCMs [182–184].

| | Organic PCMs | Inorganic PCMs |
|---|---|---|
| Advantages | • Not corrosive<br>• Low or no sub-cooling<br>• Chemically and thermally stable<br>• No segregation | • Greater phase change enthalpy<br>• Good availability, hence low cost |
| Disadvantages | • Lower phase change enthalpy<br>• Low thermal conductivity<br>• Flammability<br>• Poor thermal conductivity | • Sub-cooling due to super-saturation<br>• Corrosive<br>• Phase separation<br>• Lack of thermal stability<br>• High volume change<br>• Nucleating agents needed, yet inoperative after repeated cycling |

outer cylinder, as shown in Fig. 15 [186,187]. Three modes of cylindrical PCM container configurations are distinguished:

○ The first model designates the pipe model where the PCM fills the shell and the heat transfer fluid flows through a single tube as shown in Fig. 15a [186,188–191];
○ In the second model, the PCM fills the tube and the heat transfer fluid flows in the shell parallel to the tube as shown in Fig. 15b [189,192,193]. It has a shorter duration for melting with lower rate of heat loss to the environment because most heat supplied from the centre ends up heating the PCM; and
○ The third cylinder model is the shell and tube system as shown in Fig. 15c [188,191], which is commonly used to improve heat transfer in PCMs for its superior performance, with a PCM in the shell and heat transfer fluid in the tubes;

Further heat enhancement techniques include finned tubes with different configurations [185,190,194–199], bubble agitation [200], insertion of a metal matrix into the PCM [201,202] and the use of PCMs dispersed with high conductivity particles [203].

The encapsulations of PCMs, classified as micro-encapsulation and macro-encapsulation, can provide another interesting option. Micro-encapsulation [204,205] generally contains small PCM particles within a sealed, continuous matrix. Although micro-encapsulation have been widely studied and applied such as in the textile industry [206–211], in district energy systems [164,165,212,213] and in food industry [214], the cost of the micro-
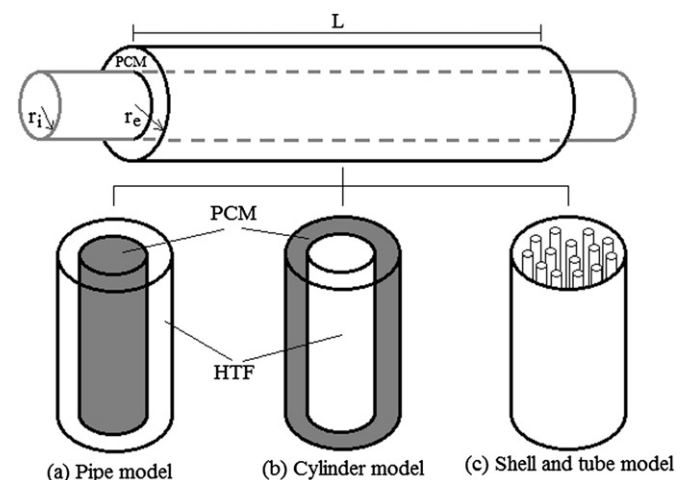


**Fig. 15.** Classification of commonly used PCM containers in terms of the geometry and configuration [178].

encapsulation system is higher compared to other storage methods. Various micro-encapsulation techniques were poignantly summarised by Hawlader et al. [205] and Boh and Sumiga [215].

On the other hand, macro-encapsulation [177] 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. 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 should meet the requirements of strength, flexibility, corrosion resistance and thermal stability [179] as: (i) they act as a barrier to protect the PCM from harmful interaction with the environment, (ii) they provide sufficient surface for heat transfer, (iii) they are easy to handle, and (iv) they provide structural stability.

### 2.3.3. Summary

The thermal energy storage medium is important since its application may improve the performance of energy systems. It is defined into two categories: sensible thermal energy storage and latent thermal energy storage with phase change materials. Technologies using sensible thermal energy storage include:

- 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 pressurised tanks.
- Use of underground aquifers as natural water and thermal energy storage; and
- Application of solar ponds where heat is stored at the bottom of the pond.

Phase change materials (PCMs) are actively researched in order to improve their heat transfer characteristics, which could be achieved by:

- using finned tubes of different configurations in heat exchangers;
- bubble agitation;
- insertion of a metal matrix into the PCM;
- using PCMs dispersed with high conductivity particles;
- shell and tube (multi-tubes); and
- encapsulation to improve heat transfer:

## 3. Conclusions

Selected low grade heat technologies were reviewed in this paper, including: (i) chemical heat pumps, (ii) thermodynamic cycles, and (iii) thermal energy storage and corresponding media to balance demand on electricity, cooling and heating cycles. To summarise, the performance improvement of chemical heat pumps can be achieved by various approaches applicable to different cycles, i.e. (gas–solid) adsorption cycles and (liquid–gas) absorption cycles. A number of promising techniques and technologies to improve heat transfer efficiency and reduce intermittency in chemical heat pumps have been summarised. A few thermodynamic cycles that are capable of converting low grade heat into electricity were also reviewed. Although much work has been done on the selection of working fluids of ORCs, there is still a lack of research into the application of working fluids of SRCs and TLCs. Compared to ORCs, both SRCs and TLCs have the potential to show better energy and exergy performances. Zeotropic working fluids and the expanders represent another two promising areas of research need. Last but not least, the thermal energy storage

medium is important since its application may improve the performance of energy systems. Such systems are defined into two categories: sensible thermal energy storage and latent thermal energy storage with PCMs. The storage of the former is usually larger but simpler whereas that of the latter may have higher energy density but limited by its poor thermal conductivity. For this reason, a few methods to improve thermal conductivity were reviewed in this paper.

Apart from the necessary improvements associated with each of the aforementioned thermal technologies, integration of these technologies will also be an important focus. The integration of thermal energy storage such as PCMs and solar ponds with thermodynamic cycles appear to pique the interest of the researchers. Absorption and adsorption cycles should also be integrated into CHP for tri-generation in circumstances where cooling or refrigeration is desired. Hybridisation of $NH_3–H_2O$ absorption system with deep geothermal ground source heat for district heating has already been applied in Denmark. More information will be presented in another paper(s) on technology roadmap for thermal energy management due to the scope limitations of this paper. Optimally utilising low grade heat is of crucial importance and therefore equal priorities should be given to all low grade heat sources (waste or otherwise) from the process industries, geothermal, solar and transport.

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