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# Reprint of "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.

#### ABSTRACT

Keywords: Chemical heat pump Thermodynamic cycle Energy storage Low grade heat

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.

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#### 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

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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 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

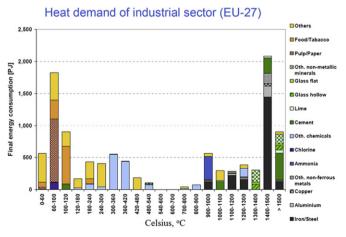


Fig. 1. Temperature distribution of industrial heat in EU-27 in 2009 [10].

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 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:

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