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Heat Pumps for Efficient Low Grade Heat Uses: From Concept to Application

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Abstract

Utilization of the widely available low grade heat including the solar thermal energy, waste heat and even the ambient heat offers great opportunities for environmentally friendly energy harvesting. Despite the efforts on developing new low grade heat conversion technologies, heat pump is still one of the most effective ways to utilize low grade heat in the current stage. Regarding the heat pump for efficient low grade heat uses, this paper unrolls a comprehensive view from the thermodynamic cycle, working medium, as well as heat and mass transfer enhancement, to the low grade heat utilization systems. Different heat pumps including vapor compression heat pump, absorption heat pump, and adsorption heat pump are included. The aim of this paper is to share our experience in the evolution from heat pump concept to low grade heat utilization. It is also helpful for researchers who try to build a bridge between thermal science and thermal engineering.

Key Words: *Heat pump, Waste heat recovery, Thermodynamic cycle, Heat and mass transfer*

1 Introduction

Low grade heat typically refers to the heat with temperature lower than 150 °C. Except for the widely available low grade heat from solar collector and geothermal well, large amount of industrial waste heat also offers great opportunities for low grade heat utilization. Among the waste heat with different forms and temperature levels, nearly half of it belongs to the low grade heat. Significant energy savings and emission reduction could be achieved if the low grade heat could be recovered. However, the low grade heat is difficult to be used due to its poor ability for power conversion. Even the low temperature heat-to-power conversion systems including the organic Rankine cycle and Kalina cycle are not efficient especially for the driving temperature below 100 °C. In this case, various new approaches have been proposed aiming at the low grade heat recovery including the thermoelectric system, pyroelectric system, thermogalvanic system, etc. However, these systems are either in the concept level or too expensive for large scale applications. Heat pumps (HPs) converting the low grade heat into high temperature heat output or low temperature cooling output are still the most effective way to utilize the low grade heat.

The researches of HPs cover the thermodynamic concept innovation, working pair selection, heat and mass transfer enhancement and its integration into waste heat recovery systems. In this paper, we will give a comprehensive view of HPs on all these aspects as presented in Fig. 1, which illustrates how to develop practical systems from the original concepts. The most commonly used HPs including the vapor compression, absorption, and adsorption HPs will be introduced. The complete technology evolution of HPs could also provide a guideline for the future development of other low grade heat utilizing approaches.

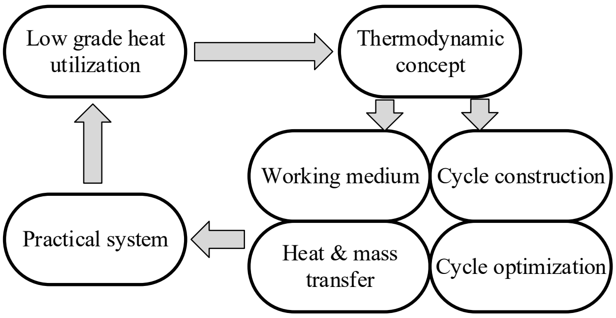

Fig. 1. Development of low grade heat utilizing technology: from concept to application.

Before specifying HP technology, the discussion starts from the ideal HP cycles for low grade heat utilization as shown in Fig. 2. The ideal HP cycle with double heat sources shown in Fig. 2(a) is the reverse Carnot cycle. By consuming work input, it could capture the low grade heat with temperature of T_r and deliver heat output at a higher temperature of T_h. The ideal HP cycle with triple heat sources shown in Fig. 2(b) is the cascading of the Carnot cycle between high temperature heat source (T_h) and medium temperature heat source (T_o), and the reverse Carnot cycle between medium temperature heat source (T_o) and low temperature heat source (T_r). Work output from the Carnot cycle will be delivered to the reverse Carnot cycle. In the ideal three-heat-source HP

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cycle, the low grade heat could act as either the high temperature heat source or low temperature heat source, depending on the temperature level of low grade heat and user demands. Other ideal HP cycles with triple heat sources could also be built by different combinations between Carnot cycle and reverse Carnot cycle, aiming for different kinds of low grade heat utilization.

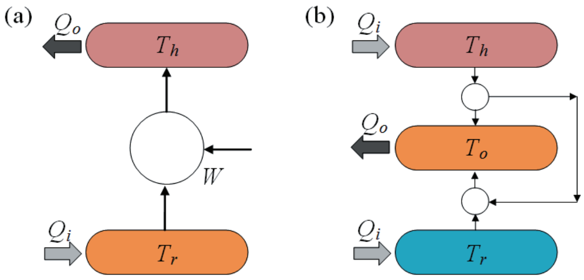


Fig. 2. Ideal cycle of HPs: (a) HP cycle with double heat sources, (b) HP cycle with triple heat sources.

With such ideal cycles of HPs, we can easily find the importance of heat and mass transfer enhancement by considering different temperature differences between the heat source and the process in the ideal cycle. Fig. 3 shows the performance degradation of HP cycle with triple heat sources. The ideal refrigeration cycle under heat source temperatures of 80 °C/30 °C/10 °C and heat transfer temperature differences of 0 °C/0 °C/0 °C could yield a refrigeration COP of 2.0. However, if the heat transfer temperature differences are increased to 10 °C/10 °C/5 °C which is common in real systems, the ideal COP will be decreased to 0.69. If the heat and mass transfer could be enhanced to minimize the temperature difference in a reasonable and economical way, the total efficiency would increase a lot.

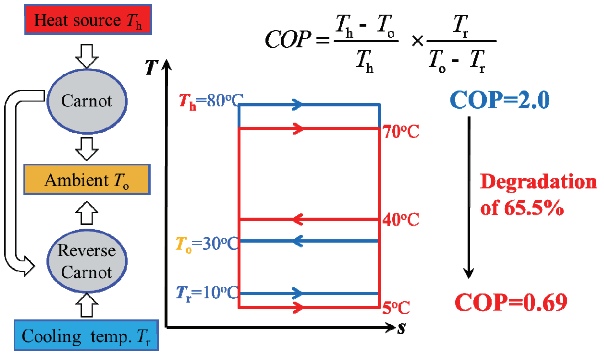


Fig. 3. Efficiency of ideal HP cycle with triple heat sources and its degradation with external heat exchange losses.

Except for the ideal HP cycles, we still need proper working media to realize these cycles, and the integration of working medium into HP cycle also brings next-step researches including the detailed cycle construction and heat/mass transfer enhancement based on the property of working media. In the following sections, the vapor compression HP will be introduced as an example of HP cycle with double heat sources, and sorption (absorption and adsorption) HPs will be introduced as examples of HP cycles with triple heat sources.

2 Vapor compression heat pump

By consuming electricity input, vapor compression HPs capture the low temperature heat in the evaporator and output the high temperature heat from the condenser. The output temperature generally ranges from 55 to 120 °C, depending on the temperature of low grade heat input. Vapor compression HP has drawn a lot of attentions in the last decades due to its decreasing investment and increasing efficiency. Currently, the vapor compression HP still needs to be improved on two aspects. (1) Applications of vapor compression HP for low grade heat utilization mainly emphasize on the industrial waste heat recovery, and high temperature vapor compression HP is favorable since heat output at higher temperatures could meet more user demands. New working fluids and the corresponding compressors, heat exchange technologies for high temperature operation should be developed. (2) Another important task for vapor compression HP is the alternative refrigerants for environmental protection. The commonly used refrigerants like R134a will be phased out in the near future. Alternative working fluid with low Global Warming Potential (GWP) or even natural fluid and the corresponding compressors, heat exchange technologies should be developed. Considering the aforementioned situation, we will discuss more about the **working medium** in this section.

2.1 Working medium of vapor compression HP

Taking the environmental issues and high temperature applications into consideration, properties of low GWP refrigerants for high temperature operation are focused in this section. Table 1 presents a comparison of selected refrigerants for high temperature vapor compression HPs. Among these refrigerants, R1234yf, R1234ze(E), R1234ze(Z), R1233zd(E) are relatively new refrigerants (Brown et al., 2009; Sánchez et al., 2017), while R152a, R717, R600 and R744 are conventional refrigerants.

In the current stage, R134a and R245fa are still popular for high temperature vapor compression HPs. However, R134a and R245fa have high GWP values, and HFOs including R1234ze(E), R1234ze(Z), and R1233zd(E) are studied as substitutions.

Natural refrigerants also have low GWP values and are typically cost effective, but most of them also has their own drawbacks. (1) R717 (ammonia) demonstrates excellent thermo-physical properties, but it has the toxic and flammable issues. (2) R600 (butane) could cover a wide range of high temperature applications with low GWP value and high critical temperature of 154 °C. However, the flammability limits its application in small plants. (3) R744 (CO_2) has a low critical temperature, which makes its operating pressure much higher than other refrigerants. (4) R718 (water) is easy to be obtained and has excellent thermo-physical properties. Therefore, high temperature vapor compression HP with R718 refrigerant is promising. However, there are still a lot of obstacles to be overcome including its low pressure, high specific volume, and immiscibility with lubricant oil.

Table 1. Properties of the low GWP refrigerants (Lemmon et al., 2013).

Refrigerants	Formula	GWP100	NBP (°C)	T_{crit}(°C)	P_{crit} (MPa)	Safety
R-152a	$C_2F_2H_2$	124	-24.0	113.3	4.52_a	A2
R-134a	CF_3CH_2F	1430	-26.1	101.06	4.06	A1
R-1234yf	$C_3F_4H_2$	4	-29.45	94.7	3.38_a	A2L
R-1233zd(E)	$C_3H_2F_3Cl$	1.4	18.26	166.5	3.63	A1
R-245fa	$CF_3CH_2CHF_2$	950	15.3	154.01	3.65	B1
R-1234ze(E)	$C_3F_4H_2$	6.0	-18.95	109.37	3.64	A2L
R-1234ze(Z)	$C_3F_4H_2$	1.4	9.745	150.12	3.54	A2L
R-600	C_4H_{10}	<1	-0.5	152.0	3.81	A3
R-744	CO_2	1	-57	31.1	7.38	A1
R-717	NH_3	<1	-33	132.3	11.33	B2
R-718	H_2O	0.2	99.9	373.95	22.06	A1

Fig. 4 demonstrates the COP of vapor compression HPs with different refrigerants and different condensation temperatures. It is indicated that COP ranges from 4.234 to 5.747, under the temperature lift of 45 °C. R1234ze(Z) shows the best performance when condensation temperature is lower than 105 °C. When condensation temperature is higher than 105 °C, R1233zd(E) is the better choice. Considering the similar COP and working temperature ranges, R134a can be replaced by R1234ze(E), and R245fa can be replaced by R1234ze(Z)/R1233zd(E) for lower GWP.

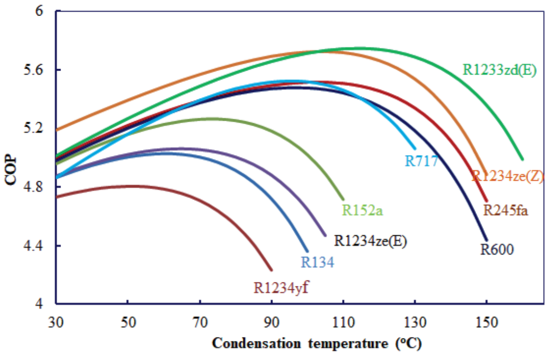
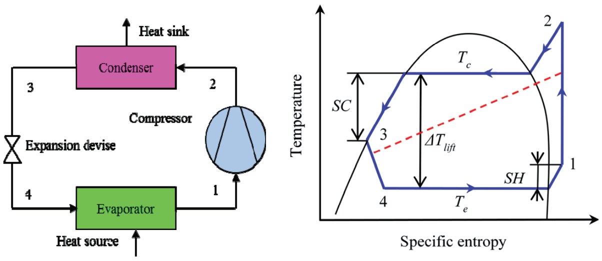


Fig. 4. COP *vs.* condensation temperature for vapor compression HP with single stage cycle, temperature lift (T_c - T_e) of 45 °C, superheating of 3 °C, and sub-cooling of 5 °C.

2.2 Cycle construction of vapor compression HP

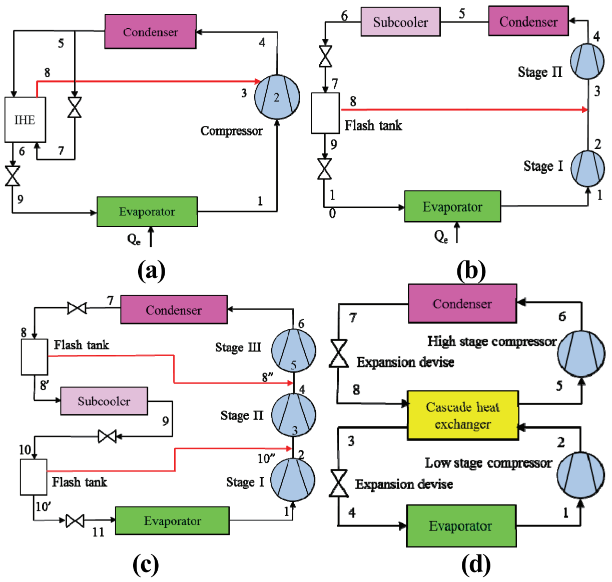
As shown in Fig. 5(a), the basic construction of vapor compression HP cycle consists of a compressor, an expansion valve and two heat exchangers i.e. the evaporator and condenser. The state variation of refrigerant on *T–s* (temperature–entropy) diagram is shown in Fig. 5(b). In the evaporator, liquid refrigerant is evaporated by absorbing low temperature heat. Then the superheated vapor is compressed and condensed in the condenser. The liquid refrigerant then passes through the expansion valve with reduction of pressure and returns to the evaporator, thus completing a full cycle. In this cycle, thermal energy at the evaporation temperature (waste heat) is upgraded to that at the condensation temperature. The output heat with higher temperature can be used for various industrial heating applications. The steady-state performance of a vapor compression HP cycle is evaluated by coefficient of performance (COP) defined as COP = Q_h/W_t, where Q_h is the heat output power and W_t is the work/electrical input power.



(a) (b)

Fig. 5. Working principle of the vapor compression HP: (a) schematic diagram, (b) *T–s* diagram (Hu et al., 2018).

In order to achieve higher efficiency or lager temperature lift, vapor compression HP could be improved by different cycle constructions. Fig. 6 shows several advanced vapor compression HP cycles, including vapor injection cycle with a flash tank for internal heat recovery (Fig. 6(a)), the two-stage compression cycle (Fig. 6(b)), the three-stage compression cycle (Fig. 6(c)) and cascading compression cycle (Fig. 6(d)). For vapor injection cycle, heat of refrigerant vapor at the outlet of the condenser can be recovered by a flash tank, thus improving the overall performance. Two-stage and three-stage cycles use two or three compressors to achieve higher temperature lift. To achieve higher temperature lift, cascading cycles use the condensing heat output of one cycle to serve as the heat input into evaporator of another cycle, and each cycle could use different refrigerants to achieve the best performance. In these cycles, various compressors including centrifugal compressor, screw compressors, turbo compressor, roots compressor, reciprocating compressor and rotary compressor could be used depending on the temperature lift, output temperature, capacity and other requirements.



(a) (b) (c) (d)

Fig. 6. Advanced vapor compression HP cycles: (a) vapor injection cycle, (b) two-stage compression cycle, (c) three-stage compression cycle, (d) cascading compression cycle (Hu et al., 2017).

2.3 Extension to three-heat-source HP

A three-heat-source HP cycle shown in Fig. 2(b) can be formed by combining the organic Rankine cycle with vapor compression HP cycle for low grade heat driving heat pumping or refrigeration. Here we take an example of turning waste heat into power, e.g. organic Rankine cycle, for vapor compression air-conditioning. For the heat source temperature, ambient temperature and cooling temperature of 150 ºC, 30 ºC and 5 ºC respectively, organic Rankine cycle and vapor compression refrigeration cycle have efficiency of ~15% and ~4.0, and the overall efficiency of such combination is ~0.6. Due to that the organic Rankine cycle cannot work efficiently under low driven temperature, this is not an efficient and flexible combination for low grade heat utilization especially when the heat source has a temperature below 150 ºC.

Alternatively, if a heat source with temperature of 150 ºC is used to power the double effect absorption chiller, a cooling COP over 1.2 could be reached. Thus, to achieve better performance for such three-heat-source heat pump or refrigeration, sorption HPs including the absorption HPs and adsorption HPs are better choices due to their different vapor compression processes.

3 Absorption heat pump

Compared with vapor compression HPs, absorption HPs upgrade the heat with the cost of low grade heat input other than electricity input, which could cover a wide temperature range of waste heat. Based on the different functions, absorption HPs could be classified into two main types, i.e. heat-amplifying type and temperature-boosting type.

Heat-amplifying absorption HP (known as the 1st type HP) is driven by high temperature heat. When the input low grade heat has temperature of 30–50 °C, the HP is able to deliver heat output of 70–95 °C, and the heating COP is always higher than 100%.

Temperature-boosting absorption HP (known as the 2nd type HP, or heat transformer) uses medium temperature heat input to yield high temperature heat output, while releasing some low temperature heat to ambient heat source. With heat input at 70–90 °C, heat output at 90–150 °C could be realized, and the COP for this case is always below than 100%.

Researches about absorption HP cover the advanced thermodynamic cycles, working pairs and enhancement of heat and mass transfer. Since working pairs of absorption HP has been widely investigated, it is not necessary to discuss this too much, and we will discuss more about the **cycle construction** and **cycle optimization** in this section.

3.1 Working medium of absorption HP

Working medium of the absorption HPs is composed of the refrigerant and the absorbent. Various working pairs have been investigated for obtaining better performance, higher temperature lift capability, wider working temperature range, lower crystallization risk, and so on. Absorption working pairs can be classified according to the refrigerants as shown in Table 2. The first type of working pairs is based on water, which is always an excellent choice for heat sink with temperature higher than 0 °C. Salt solution or lye will serve as the absorbents (such as LiBr). The second type of working pairs is based on ammonia, which is a natural refrigerant able to work efficiently below 0 °C. Water, salt or aqueous solution of slat can be the absorbents. The third type of working fluids is based on organic refrigerants including R32, R124, R134a and TFE, the absorbents are also organic fluids like DMAC, DMEU, NMP and E181. Among these working pairs, LiBr-water and water-ammonia are the most popular options.

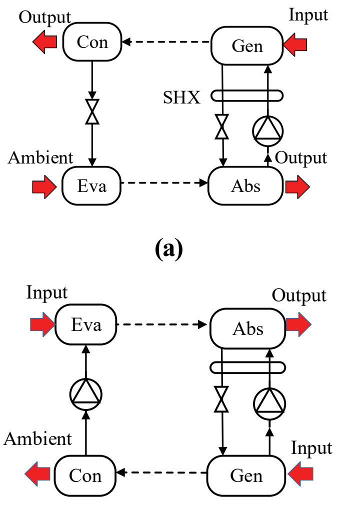
Table 2. Working pairs for absorption HPs (Xu and Wang, 2017a).

Refrigerants	Absorbents
Water	LiBr, LiCl, $CaCl_2$, LiBr + $LiNO_3$, LiBr + CH_3COOK, NaOH + KOH,
Ammonia	H_2O, $LiNO_3$, NaSCN, H_2O + LiBr
R32, R134a	DMAC, DMEU, NMP, DMETEG
TFE	E181, NMP, PYR

3.2 Cycle construction of absorption HP

Absorption HPs may use different cycles such as single effect cycle, double effect cycle, double lift cycle and variable effect cycle according to the heat source and heat sink temperatures (Xu and Wang, 2016). Absorption HP (heat-amplifying type) requires high temperature heat input in generation process and delivers heat output in absorption and condensation process as shown in Fig. 7(a) (Gen, Con, Abs and Eva represents generation, condensation, absorption and evaporation, respectively). The evaporation process is usually heated by ambient or waste heat. Compared with the heat input, the heat output has a lower temperature and larger capacity, which results in COP (total heat output/high temperature heat input) higher than 100%. This type of absorption HP is usually employed for heating supply and domestic hot water supply. Typical single effect LiBr-water absorption HP has temperature lift of ~50 °C with theoretical COP about 1.7 (Xu and Wang, 2017a). A boiler based on burning of oil or natural gas can act as the heat source, but waste heat from industrial processes or power plant is a better choice.

Temperature-boosting type absorption HP is usually referred as absorption heat transformer as shown in Fig. 7(b). It requires heat input in generation and evaporation processes, and supplies heat output in absorption process. Condensation process is usually cooled by ambient heat sink. Compared with heat input, heat output has a higher temperature but smaller quantity resulting in COP (high temperature heat output/total heat input) lower than 100%. As absorption heat transformer is able to produce heat output of 100 °C or higher, it has more potential applications in industrial processes. Typically, the heat input temperature is about 60–90 °C and heat output temperature is about 100–130 °C. A common temperature lift of 70–100 °C can be achieved compared with ambient temperature, and COP of 0.4–0.5 could be achieved (Xu and Wang, 2017a).

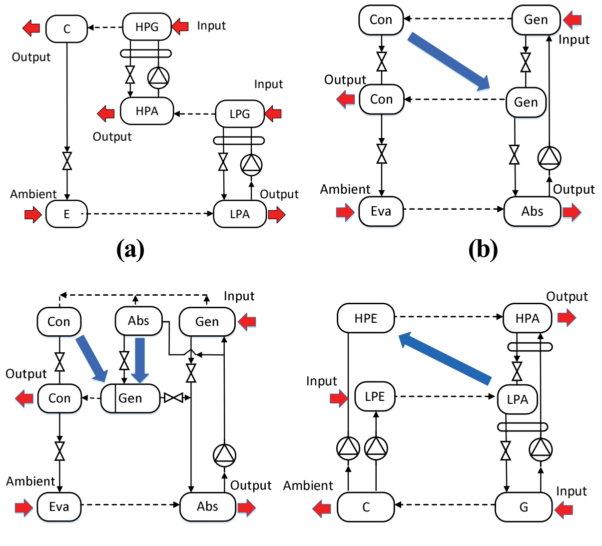


(a)

(b)

Fig. 7. Single effect absorption HP cycles: (a) heat-amplifying type, (b) temperature-boosting type.

To fulfill different demands of temperature lift, various advanced absorption HP cycles for both heat-amplifying and temperature-boosting have been proposed (Xu and Wang, 2017a), and some of the examples are shown as follows. (1) For larger temperature lift of heat-amplifying or lower driving temperature, double lift absorption HP cycle can be used as shown in Fig. 8(a). Theoretically, temperature lift of 50 °C can be achieved under driving temperature of ~90–130 °C with COP of 1.3. (2) For better utilization of heat source with higher temperature, double effect absorption HP cycle can be used to improve the efficiency as shown in Fig. 8(b). It requires higher driving temperature than the single effect cycle for the same temperature lift. Temperature lift of ~30 °C can be achieved with COP of ~2.3. (3) For temperature lift between single effect cycle and double effect cycle, the variable effect absorption HP cycle shown in Fig. 8(c) can be used. Its temperature lifting ability is between the single effect cycle and double effect cycle, and the theoretical COP varies from 1.7 to 2.3 (Xu et al., 2013). (4) For higher temperature lift with temperature-boosting, double absorption heat transformer can be used as shown in Fig. 8(d). Temperature lift can be increased by 50–60% in comparison with the single stage configuration, however, its COP will be decreased to 0.25–0.4.



(a) (b)

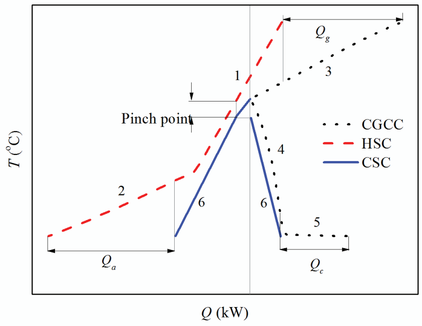
(c) (d)

Fig. 8. Advanced absorption HP cycles: (a) double lift cycle, (b) double effect cycle, (c) variable effect cycle, (d) double absorption heat transformer (Xu and Wang, 2017a).

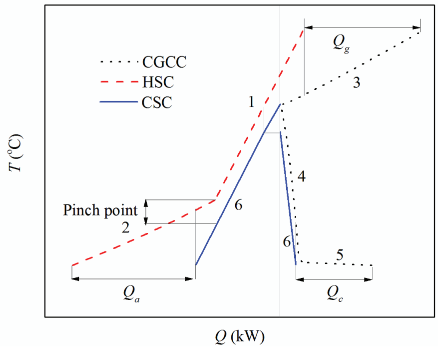
3.3 Cycle optimization with internal heat recovery

Compared to the LiBr-water absorption HPs, water-ammonia absorption HPs have advantages such as the applications at the evaporation temperature below 0 °C and easier maintenance because of the positive system pressure. Moreover, it is superior for heat output with temperature glide due to its large concentration glide (corresponding to the saturation temperature) in the absorption process. However, the system configuration is more complicated due to the rectification process, and the efficiency strongly depends on the system configuration. In this case, cycle optimization is essential, and it can be achieved through internal heat recovery.

The authors analyzed the optimal internal heat recovery strategies of heat-amplifying water-ammonia heat pumps by pinch technology. According to different operating conditions, three strategies of internal heat recovery, named as Split cycle 1, Split cycle 2, and GAX cycle, are obtained as shown in Fig. 9 (Du et al., 2014, 2015). In the figure, CGCC, HSC, and CSC respectively represent the distillation column grand composite curve, the hot stream curve and the cold stream curve, which shows the correlation between the heat load and the temperature. Curves 1 to 6 represent the weak solution (low percentage of ammonia) from the generator, absorption process, generation process, rectification process, condensation process and the strong solution from the absorber, respectively. The overlapped portion between the curves is the internal heat recovery process, and the projected length on the horizontal axis indicates its heat load. It can be found that absorption heat has a larger temperature glide than the condensation heat. As a result, the hot water could be heated to a higher temperature. By applying such cycle optimization, the optimized absorption cycle including Split cycle 1, Split cycle 2 and GAX cycle could be derived under different conditions, and COP enhancement of 20–90% could be achieved (Du et al., 2014).



(a)



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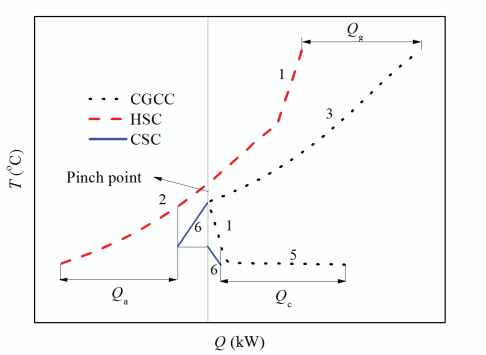

(c)

Fig. 9. Three strategies for the internal heat recovery of water-ammonia absorption HPs: (a) split cycle 1, (b) split cycle 2, (c) GAX cycle (Du et al., 2014).

4 Adsorption heat pump

The adsorption HP shares the same thermodynamic concept with the absorption HP due to the similarity between absorption process and adsorption process. Sometimes, absorption systems and adsorption systems are collectively termed as sorption systems. The difference is that adsorption process utilizes solid-gas working pairs, which makes the cycle construction and heat/mass transfer totally different. The use of solid-gas working pair also makes the adsorption free of pumping process, which is favorable for small scale application. Besides, a lot adsorption working pairs are available, which offers the possibility for lower driven temperature utilization.

Different from the liquid working medium used in vapor compression HPs and absorption HPs, solid porous medium is used as adsorbent in adsorption system, which makes the heat and mass transfer enhancement more important. In this case, we will discuss more about the **heat and mass transfer enhancement** in this section.

4.1 Working medium of adsorption HP

The working pair of adsorption HP consists of the refrigerant/adsorbate and the adsorbent. Water, methanol and ammonia are the most commonly used refrigerants (Wang et al., 2014b), which are all environmental-benign substances with large latent heat of vaporization. Methanol and ammonia have low freezing point which are suitable for subzero evaporation conditions. For typical working temperatures, water and methanol need vacuum environment while ammonia works under high pressure. Methanol and ammonia are combustible and toxic, so they are not suitable for applications where high safety requirement is required. Methanol also takes a risk of decomposition, so its application is generally limited below 120 °C.

Various adsorption working pairs have been proposed based on water, ammonia and methanol, which could be classified into two types based on the adsorption mechanism, i.e. physical adsorption and chemisorption. Due to the need of simultaneous heat and mass transfer, porous medium is typically used as the adsorbent. Table 3 shows several commonly used working pairs.

Table 3. Comparison of common working pairs for adsorption HP.

Working pair	Silica gel-water	Zeolite-water	Activated carbon-methanol	Activated carbon-ammonia	$CaCl_2$-ammonia
Adsorption heat (kJ/kg)	2800	3300–4200	1800–2000	1700	2200–2300
Driving temperature	< 100 °C	> 150 °C	80–120 °C	80–200 °C	100–150 °C
Condensation temperature	30–45 °C	wide range	20–50 °C	20–50 °C	20–50 °C
Evaporation temperature	> 0 °C	> 0 °C	Could be < 0 °C	Could be < 0 °C	Could be < 0 °C

Silica gel-water is the most common working pair for adsorption HP. Its adsorption heat is ~2800 kJ/kg and desorption temperature can be as low as 50 °C. Working temperature of silica gel should be lower than 120 °C, otherwise silica gel would lose the adsorption ability. Typically, a silica gel-water adsorption chiller could work efficiently under driving temperature, condensation temperature, and evaporation temperature of 80 °C, 30–45 °C, and 5–10 °C, respectively.

Since zeolite-water is stable at high desorption temperature, it can be used to utilize heat above 200 °C. Its adsorption heat is 3300–4200 kJ/kg, which is higher than that of silica gel-water pair, resulting in a longer cycling period. Zeolite-water working pair can operate with similar performance in a large range of condensation temperature since its adsorption isotherm curves are quite insensitive to condensation pressure. The typical working conditions of a zeolite-water adsorption chiller has driving temperature, condensation temperature, and evaporation temperature of 180 °C, 30–80 °C, and 5–10 °C, respectively.

Adsorption heat of activated carbon-methanol is 1800–2000 kJ/kg, which is lower than that of the previous working pairs. Activated carbon-methanol can be driven by heat source at below 100 °C, which makes it suitable for low temperature heat recovery. The typical working conditions of activated carbon-methanol adsorption chiller have driving temperature, condensation temperature, and evaporation temperature of 80–120°C, 20–50 °C and -10–10°C, respectively.

Activated carbon - ammonia is another commonly used working pair. Its adsorption heat is ~1700 kJ/kg. Due to the higher operation pressure of activated carbon–ammonia pair, cycling period could be reduced due to the improved mass transfer. Activated carbon - ammonia has a wide range of driving temperature from 80 to 200 °C. However, limited by the high pressure risk of ammonia system, condensation temperature of activated carbon - ammonia system should not be higher than 50°C. The typical working conditions of activated carbon-ammonia adsorption refrigeration has driving temperature, condensation temperature, and evaporation temperature of 80–200°C, 20–50°C and -20–10°C, respectively.

Unlike the above physical adsorbents, metal halides belong to the chemical adsorbent when they work with ammonia. $CaCl_2$ is the most commonly used sorbent for chemisorption HP. Actually, reaction of $CaCl_2$ and ammonia has three stages, in which $CaCl_2{\cdot}2NH_3$, $CaCl_2{\cdot}4NH_3$ and $CaCl_2{\cdot}8NH_3$ are the products of every stage. Adsorption heat of $CaCl_2$-ammonia is about 2200–2300 kJ/kg while adsorption quantity (amount of refrigerant per unit adsorbent) of $CaCl_2$-ammonia can reach 1.22 kg/kg, which is much higher than that of the physical adsorption working pairs. $CaCl_2$-ammonia working pair requires high driving temperature and medium level condensation temperature. The general working conditions of $CaCl_2$-ammonia adsorption chiller has driving temperature, condensation temperature, and evaporation temperature of 100–150 °C, 20–50 °C and -20–10 °C, respectively. The main disadvantages of metal halides-ammonia working pair are the swelling and agglomeration phenomena during repeated adsorption and desorption processes, which causes the heat and mass transfer degradation. To solve these problems composite sorbents of metal halides and porous matrix (such as activated carbon and expanded graphite) are developed and will be discussed later.

The above examples of working conditions are typically for refrigeration or air conditioning purposes, which shares the same principle for heat pumping. The differences between condensation and evaporation temperatures in refrigeration cases are the corresponding temperature lift for the adsorption HP.

4.2 Cycle construction of adsorption HP

The common configuration of adsorption HP is a two-bed system with heat recovery, mass recovery or both of them (Wang, 2001). Fig. 10 shows the schematic of an adsorption HP system with heat and mass recovery. Alternating adsorption/desorption of two adsorbers can continuously produce cooling or heating. After the adsorption/desorption modes, the system successively proceeds mass recovery and heat recovery. In the mass recovery, mass recovery valve (a bypass valve) is opened, making the pressure balanced between two adsorbers. As a result, adsorption and desorption processes are further promoted and the cycle adsorption quantity is enlarged, leading to an improved system performance. Heat recovery is achieved through circulating thermal fluid between the two adsorbers, thus sensible heat and even part of the adsorption heat could be recovered. With such heat recovery process, heat input is reduced and better performance could be achieved.

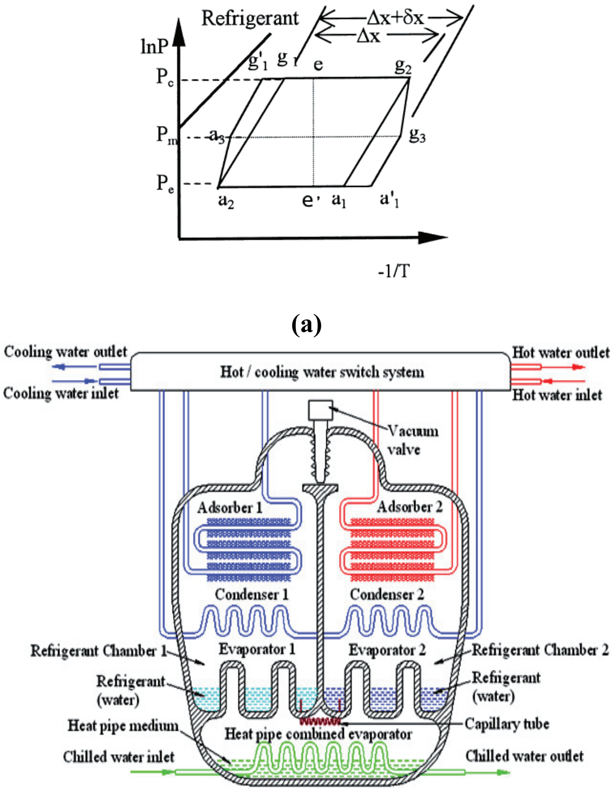

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Fig. 10. Schematic of a heat and mass recovery adsorption HP system: (a) thermodynamic cycle, (b) typical adsorption chiller design (Wang et al., 2014a).

Silica gel-water adsorption system with heat and mass recovery is one of the most developed adsorption systems which has been commercialized. Studies showed that silica gel-water HP can achieve COP over 0.5 (Pan et al., 2016) for cooling and COP of 1.3 (Núñez et al., 2006) for heating under 80–95 °C driving temperature, 35-45°C intermediate temperature and 10–20 °C low temperature. Applications of silica gel-water HP mainly include solar cooling system and combined cooling, heating and power (CCHP) system (Luo et al., 2007; Núñez et al., 2006; Zhai et al., 2007).

Another type of adsorption HP for temperature lift is the resorption HP. Resorption HP requires two or more sorption beds which are filled with different chemical sorbents (commonly metal halide-ammonia pairs). Sorption beds can act as the functions of condenser and evaporator, respectively. Schematic of a resorption HP is shown in Fig. 11. At high pressure level of P_H, low temperature adsorbent (LTS, S/G1) is regenerated by the intermediate temperature heat source (T_{in}) and releases ammonia. At the same time, high temperature adsorbent (HTS, S/G2) adsorbs ammonia and releases the heat at high temperature level of T_{out} (a temperature lift ΔT is thus created). After cooled down to a low pressure level of P_L, LTS adsorbs ammonia and releases adsorption heat to the ambient at low temperature level of T_{ad}. Meanwhile, HTS desorbs ammonia with the heating by the intermediate temperature heat source T_{in}. Various metal halide-ammonia pairs could be adopted by the resorption HP, thus meeting different requirements of temperature lift. Theoretically, $MnCl_2$-NaBr-ammonia working pair could upgrade the heat from 124 to 152 °C with COP of 0.55, $MnCl_2$-$CaCl_2$-ammonia working pair could upgrade the heat from 87 to 152 °C with COP of 0.46, and $NiCl_2$-$SrBr_2$-ammonia working pair could upgrade the heat from 130 to 259 °C with COP of 0.43 (Li et al., 2013). Research on resorption temperature lift HP is still at theoretical stage, though the refrigeration and energy storage prototypes have been established and investigated in detail (Bao et al., 2014).

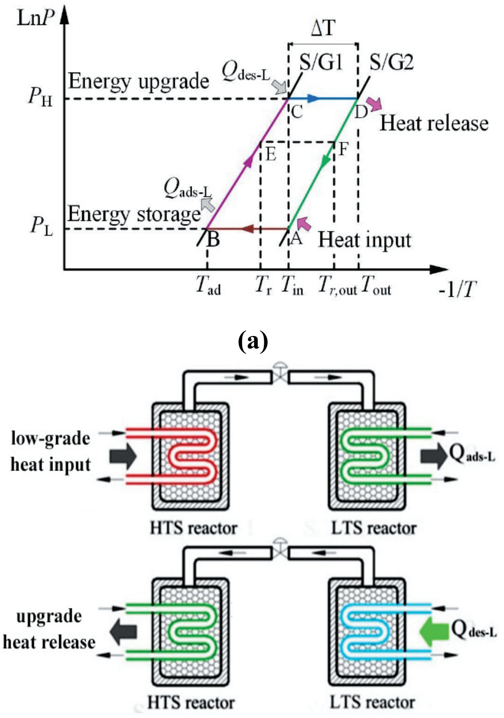

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Fig. 11. Schematic of a resorption HP system: (a) Clapeyron diagram, (b) schematic diagram (Li et al., 2013). S/G-solid/gas reaction, LTS-low temperature sorbent, and HTS-high temperature sorbent.

4.3 Heat and mass transfer enhancement of adsorption HP

As illustrated in Fig. 3, the heat and mass transfer enhancement is necessary to increase the efficiency of HP considering the external irreversible loss. Compared to the vapor compression HP and absorption HP, the heat and mass transfer enhancement in adsorption HP is more difficult since solid porous working medium is used. In the adsorption HP, there are two major issues including the stable and efficient adsorption (Wang and Wang, 1999), and the coupled heat and mass transfer enhancement. Compound adsorbent and consolidated adsorbent have been developed to address these two issues.

(1) Compound adsorbent. As discussed before, the adsorption working pair is classified into physical adsorption and chemisorption working pairs based on the adsorption mechanism. For physical adsorption, the adsorption process is stable but the adsorption quantity is low which will increase the plant size. For instance, activated carbon-methanol and silica gel-water have adsorption quantity of 0.2–0.4 kg/kg and 0.15–0.25 kg/kg respectively. On the contrary, the chemisorption typically has a high adsorption quantity, but the adsorption quantity degrades fast under long term operation. For instance, $CaCl_2$-ammonia working pair has adsorption quantity of ~1.2 kg/kg which is 3–6 times higher than that of the previously mentioned physical adsorption working pair. However, the adsorption quantity decreases ~30% after 10 times of adsorption-desorption, and the capacity of adsorption HP with such working pair degrades over 80% in half a year (Wang et al., 2005a). The reason for adsorption quantity decrease is the permeability degradation due to solidification of chemical adsorbent.

To overcome the aforementioned problems of physical adsorption and chemisorption, we proposed the use of compound adsorbent which integrates the chemical adsorbent into the pores of physical adsorbent as shown in Fig. 12. The pores of physical adsorbent offer small amount of adsorption, and more importantly, they offer stable mass transfer paths for the efficient chemisorption. Taking the pure $CaCl_2$ adsorbent as an example, its permeability decreases from 2.34×10^{-9} m^2 to 1.56×10^{-16} m^2 after repeated adsorption of ammonia. When it is integrated with activated carbon and forms the activated carbon/$CaCl_2$ compound adsorbent, the permeability decreases from 4.60×10^{-11} m^2 to 2.77×10^{-13} m^2 after repeated adsorption of ammonia. The permeability after adsorption is enhanced by 3 orders of magnitude, which ensures stable and efficient adsorption (Wang et al., 2004).

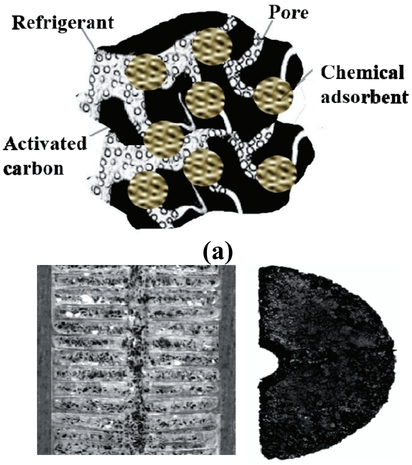

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Fig. 12. Compound adsorbent for stable and efficient adsorption: (a) schematic of the compound adsorbent, (b) activated carbon/$CaCl_2$ adsorbent compound adsorbent (Wang et al., 2004).

(2) Consolidated adsorbent. In the adsorption process, there is a conflict between the heat transfer enhancement and mass transfer enhancement. Pores inside the porous adsorbent offer the paths for mass transfer while the solid part offers the paths for heat transfer. When the pore size of the adsorbent is large, the mass transfer is enhanced but the heat transfer is depressed, and vice versa. In order to enhance the heat and mass transfer simultaneously, we developed the consolidated adsorbent (Wang et al., 2005b) in which the heat transfer of the solid part is significantly enhanced. In this case, high porosity is acceptable for both heat and mass transfer enhancement.

Fig. 13 shows the consolidated adsorbent made of $CaCl_2$ and expanded graphite treated with sulfuric acid (ENG-TSA). The expanded graphite offers both high thermal conductivity and sufficient mass transfer paths for absorption. The thermal conductivity of $CaCl_2$ consolidated with ENG-TSA is increased up to 88.1 W/(mK), which is 400 times higher than the granular $CaCl_2$ (Jiang et al., 2014).

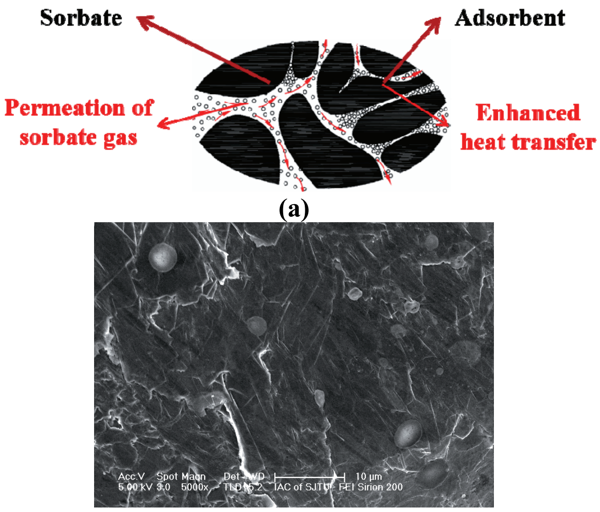

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Fig. 13. Consolidated adsorbent for simultaneous heat and mass transfer enhancement: (a) schematic of consolidated adsorbent, (b) consolidated adsorbent of ENG-TSA (Jiang et al., 2014).

5 Heat pump for low grade heat uses

In this section, the application of HPs for the utilization of typical low grade heat including industrial waste heat, transportation waste heat and solar heat is introduced to show how effective of these HP systems could be in the utilization of low grade heat.

5.1 Application of vapor compression HP

Waste heat from many industries can be recovered and upgraded into useful heat by vapor compression HP, which has great potential in energy saving and environment protection. Table 4 summarizes several cases of vapor compression HP with different refrigerants. For low temperature heat supply (< 70 °C), R134a, R410a, and ammonia are commonly used. For medium temperature heat supply (~90 °C), refrigerants of CO_2 and R245fa are suitable, and the heat output can be used for industrial manufacturing processes of slaughter house preheating and dyeing liquid heating. For high temperature heat supply (> 120 °C), R718 could be used, and again the heat is used for manufacturing processes, such as furnace drying and process heating. The better choices of refrigerants and cycles for waste heat recovery are summarized in Fig. 14. The industrial waste heat sources are listed in the range from high temperature to low temperature. The widely used refrigerants at present and corresponding low GWP refrigerants in the future are analyzed. As natural refrigerants, R744 and R717 are popular in common heating applications. R1234ze (Z) and R1233zd (E) are competitive refrigerants for R245fa and R718 which are quite attractive in high heating temperature applications due to their outstanding thermodynamic properties. Here two cases of vapor compression HP conducted by our team are introduced in detail, including a waste heat recovery system with HP and a high temperature HP with natural refrigerants.

Table 4. Application of industrial vapor compression HPs (Centre, 2014; Chamoun et al., 2012; Wu et al., 2016).

Country/ Year	Heat resource	Refrigerant/ Capacity	Output temperature	Applications
Hohenems, Austria/ 2012	Waste heat, 20 °C	R134a/ 257kW	55 °C	Cleaning and heating
Futtsu, Japan/ 2010	Waste gas, 20 °C	R410A/ 180kW	50 °C	Heating for greenhouse
Halifax, UK/ 2010	Condensation waste heat, 30 °C	NH_3/ 600kW	70 °C	Chocolate factory
China/ 2016	Dyeing waste water, 60 °C	R245fa/ 200kW	95 °C	Dyeing liquid heating
Switzerland/ 2010	Waste water, 30 °C	CO_2/ 800kW	90 °C	Slaughter house preheating
Japan/ 2012	Water of drying furnaces, 60 °C	R134a/ 627kW	130 °C	Furnaces drying
France/ 2014	Industrial waste heat, 80 °C	R718 (H_2O)/ 340kW	120 °C	Process heating

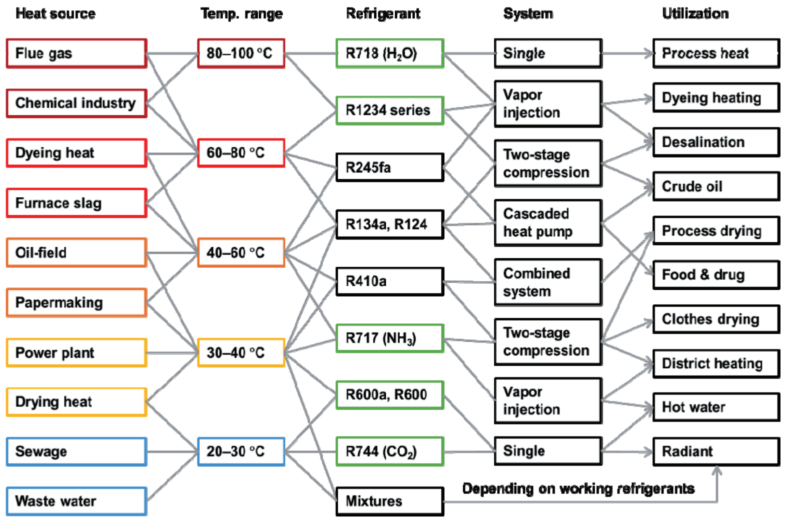

Fig. 14. Refrigerant and cycle construction choices of vapor compression HPs for waste heat recovery.

Fig. 15 shows a waste heat recovery system with large scale centrifugal vapor compression HP built in the Angang Iron and Steel Plant, located in Liaoning, China. Permanent-magnet synchronous variable-frequency centrifugal compressor was used, and the total heating capacity was 9100 kW. Heat output was used for central heating. As shown in Fig. 15 (a), a serial connection of external water loop was used to reduce the external irreversible loss and to increase the efficiency. The test results showed that COP of 6.13 was achieved under waste hot water inlet/outlet temperatures of 32.1/24.1 °C and hot water supply temperature of 62.8 °C. The results showed such serial connected HP system with gradual water heating is efficient for water heating. The waste heat recovery system with vapor compression HP could cover the heating demand of 180,000 m^2 (calculated from heating load of 50 W/m^2). The system has been working for one heating season till now, consuming 2.43 million kWh of electricity, and the cost was 1.46 million RMB. Considering that the local heating supply price per year is 22 RMB/m^2, the heating supply of 180,000 m^2 per year would cost 3.96 million RMB. The annual net profit obtained from the waste heat recovery system was about 2.5 million RMB. At the same time, by suppling hot thermal energy of 45,000 GJ from the waste heat, more than 3500 tons of standard coal were saved.

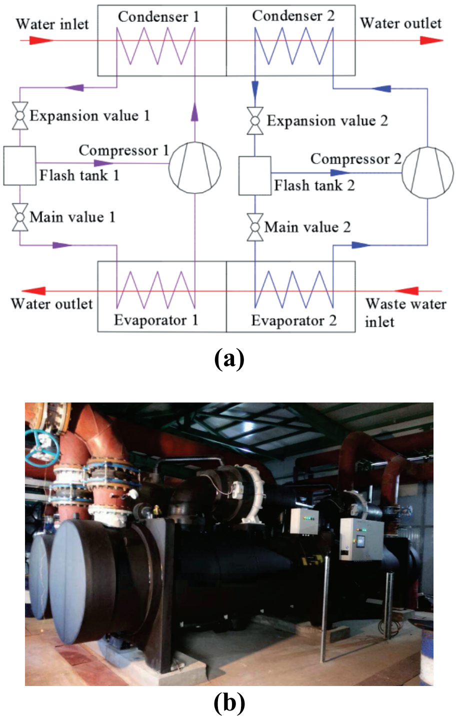

Fig. 15. Industrial waste heat recovery by large scale centrifugal vapor compression HPs: (a) schematic of the serial connected vapor compression HP system, (b) centrifugal vapor compression HP plants.

Fig. 16 shows our recently developed water vapor compression HP system developed for high temperature waste heat recovery. The twin-screw compressor was designed with three different injection ports ensuring water injection during the whole compression process. The internal compression ratio and the rotation speed of this compressor was 4.5 and 5000 rpm. The rated heating capacity of plate condenser and falling film evaporator were 300 kW and 240 kW, respectively. Experiments were conducted under steady evaporation temperature of 87 ℃ and increasing condensation temperatures from 119.6 to 126.5 ℃. Results showed that the power consumption ranged from 51.3 to 56.9 kW, the heating capacity ranged from 226.1 to 230.5 kW and the COP decreased from 4.40 to 4.03. Compared with the vapor compression HP system using R245fa, water vapor HP system has similar performance and better environmental benefit.

Fig. 16. The water vapor compression HP prototype for high temperature application.

5.2 Application of absorption HP

Absorption HP can be directly driven by low grade heat which makes it popular for solar heat utilization (Sun et al., 2015; Wang et al., 2016; Xu and Wang, 2017b; Xu et al., 2015). Fig. 17 shows one of our researches about the solar/gas driven single/double effect absorption HP system to fulfill the heating, cooling and hot water demand in a hotel (Sun et al., 2015). Solar driven single effect mode works when the solar collector provides enough heat input. In the rest time, gas driven double effect mode works to ensure the continuous operation of this system. The single effect mode and double effect mode have cooling capacities of 320 kW and 1280 kW, respectively. Year round operation showed that the integration of solar energy into this absorption HP system saved 49.7% of the natural gas consumption.

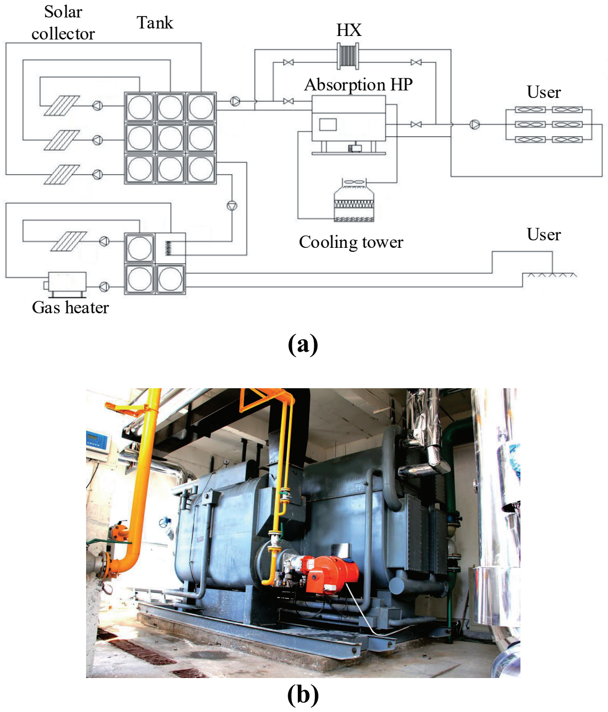

Fig. 17. Application of absorption HP for solar heat utilization: (a) schematic of the solar driving absorption heating and cooling system, (b) single/double effect absorption HP (Sun et al., 2015).

Except for the direct utilization of solar thermal power, absorption HP has another advantage which makes it suitable for waste heat recovery, i.e. large scale application (Xu et al., 2018). Both the size and cost per unit heating capacity of absorption HP will decrease with the increase of capacity. Thus absorption HP can be both efficient and cost-saving for recovering the large amount of waste heat from power plant or industrial processes. Fig. 18 shows a waste heat recovery system for power plant built in Lanzhou, China (Xu et al., 2018). Fig. 18(a) shows the schematic of the waste heat recovery system with LiBr-water absorption HP. The system consists of 6 serial absorption HP plants and each plant has a rated heating capacity of 48.46 MW. Condensation heat of power plant is recovered the absorption HPs. Heat output of the absorption HPs is used for district heating. Test results showed that the absorption HPs achieved heating capacity of 63.57 MW and COP of 1.77 under steam pressure of 0.24 MPa, waste heat temperature of 34.63 °C and hot water outlet temperature of 81.34 °C. For the year round operation, this system recovered 1.55 PJ waste heat, and reduced 6.45 × 10^8 kg of water assumption and 1.49 × 10^8 kg CO_2 emission.

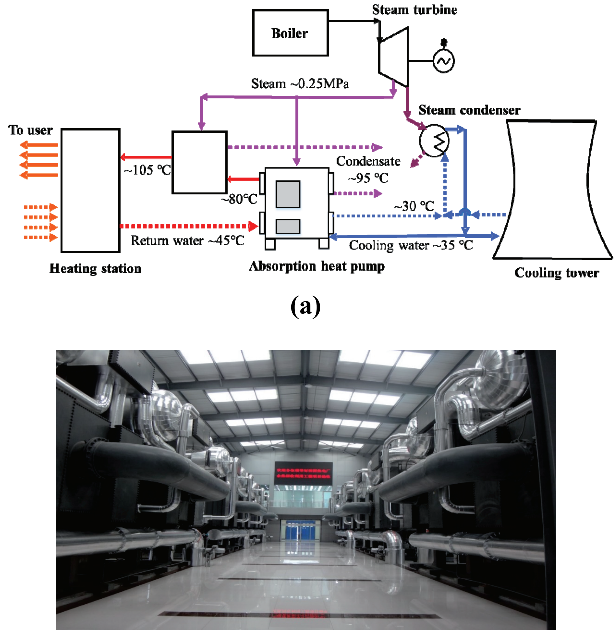

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Fig. 18. Application of absorption HPs for industrial waste heat recovery: (a) schematic of the waste heat recovery system, (b) absorption HP plants (Xu et al., 2018).

Based on cycle optimization, as stated in section 3.3, a practical water-ammonia absorption prototype is developed for freezing applications, which is driven by the exhaust of diesel engine on a fishing-boat (Du et al., 2017). According to the operating conditions of marine application, the split cycle 1, one of the three optimal strategies for internal heat recovery, is applied and it is modified in the light of the practical system construction. Moreover, the prototype is built with the design of anti-swaying, anti-corrosion and small bulk, etc. The prototype, as shown in Fig.19, produces cooling capacity of 33.8 kW and the thermal COP reaches 0.53 under the test conditions that the temperatures of the cooling water, secondary refrigerant and exhaust inlet are 26.1 °C, -15.2 °C and 567 °C, respectively. This system can be installed on a small fishing-boat with a diesel engine of 200 kW, and meet the needs of harvesting preservation. Such a system could ensure the freezing demand without taking ice cubes which is promising for small fishing boats.

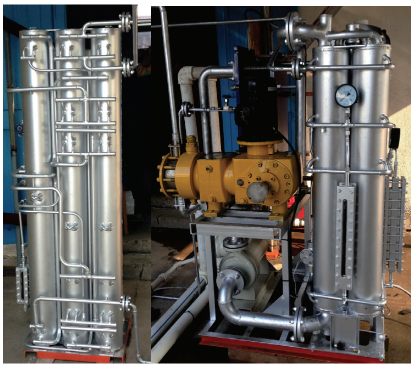
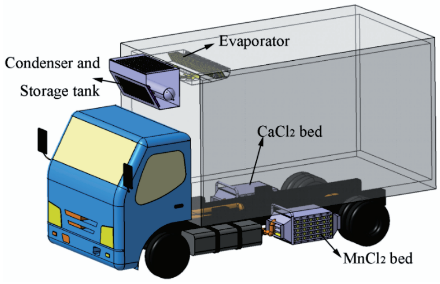


Fig. 19. Ammonia-water absorption freezer driven by diesel engine exhaust (Du et al., 2017).

5.3 Application of adsorption Refrigeration

Different from the absorption HP, adsorption HP is advantageous for small scale, air-cooled and low driven temperature conditions. Besides, it has much better anti-vibration performance than absorption HP due to the solid adsorbent used in the system. In this case, it is suitable for the waste heat recovery of diesel engine in truck or boat. Fig. 20 shows an adsorption freezing system for refrigerated truck developed by our team (Gao et al., 2016). It is driven by the heat from the exhaust gas of diesel engine, and the system provides cooling output to maintain the low temperature inside the chamber. The schematic of this adsorption freezing system is shown in Fig. 20 (b), where $MnCl_2/CaCl_2-NH_3$ two-stage adsorption cycle is adopted. Experimental results showed that this system could obtain 1.32 kW cooling output at a temperature of -10 °C when driven by exhaust gas at 270 °C, and this is enough to keep the low temperature in the chamber. The most recent updated system could even reach more than 2.5 kW refrigeration power.



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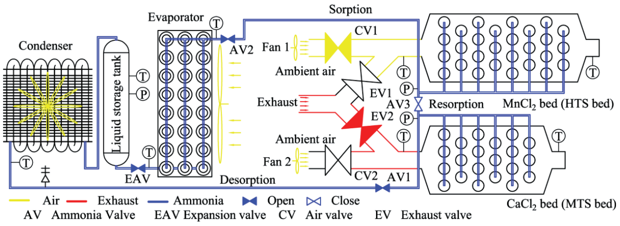

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Fig. 20. Application of adsorption HP for diesel engine waste heat recovery: (a) schematic of the waste heat recovery system, (b) schematic of the adsorption HP (Gao et al., 2016).

6 Conclusions and Perspectives

In this paper, we have shown the development of low grade heat utilizing HP system from the thermodynamic concept to the real application. (1) In the thermodynamic concept level, ideal HP cycles with double heat sources and triple heat sources offer the theoretical framework for HP system. (2) In the next step, the technical details including working medium, cycle construction, cycle optimization and heat/mass transfer enhancement for vapor compression HP with dual heat sources and absorption/adsorption HPs with triple heat sources are introduced. Due to their different features, working medium, cycle construction/optimization and heat/mass transfer enhancement are emphasized for different HPs. (3) At last, the applications of different HPs for industrial waste heat recovery, transportation waste heat recovery and solar heat utilization are introduced.

The relatively complete view of HPs technology evolution has been shown through the description of researches in these three levels. This paper also shows that plenty of chances on novel working principle, working medium, cycle construction, system optimization and heat/mass transfer enhancement are available in the future development of thermal engineering systems. As new technologies in thermal science including HPs are still being developed by many researchers, we hope such an overview of HP technology development could provide researchers how technology is developed from concept to application, and help those who want to bridge thermal science and thermal engineering.

A more general view for waste heat utilization could be shown as Fig. 21, where centralized heat could be transferred into power via Ranking cycle, organic Ranking cycle, or Kalina cycle depending on its temperature level and capacity. It could be used to generate cooling by absorption or adsorption refrigeration. It could be used directly, or upgraded by heat pump (vapor compression, absorption, adsorption, or chemical reaction). These centralized heat is turned into network electricity/heating/cooling to its customers (industrial, commercial, or residential). For those small capacity heat sources, distributed energy system network could be established by heat transmission via piping or via heat transportation with thermal storage units. The distributed localized heat could thus be turned to heating/cooling by various thermal driven systems like sorption heat pump.

The unique solution would be the unified centralized and distributed energy systems to form a smart energy network. An integrated network use of low grade heat could have great potentials for efficient energy utilization in the near future.

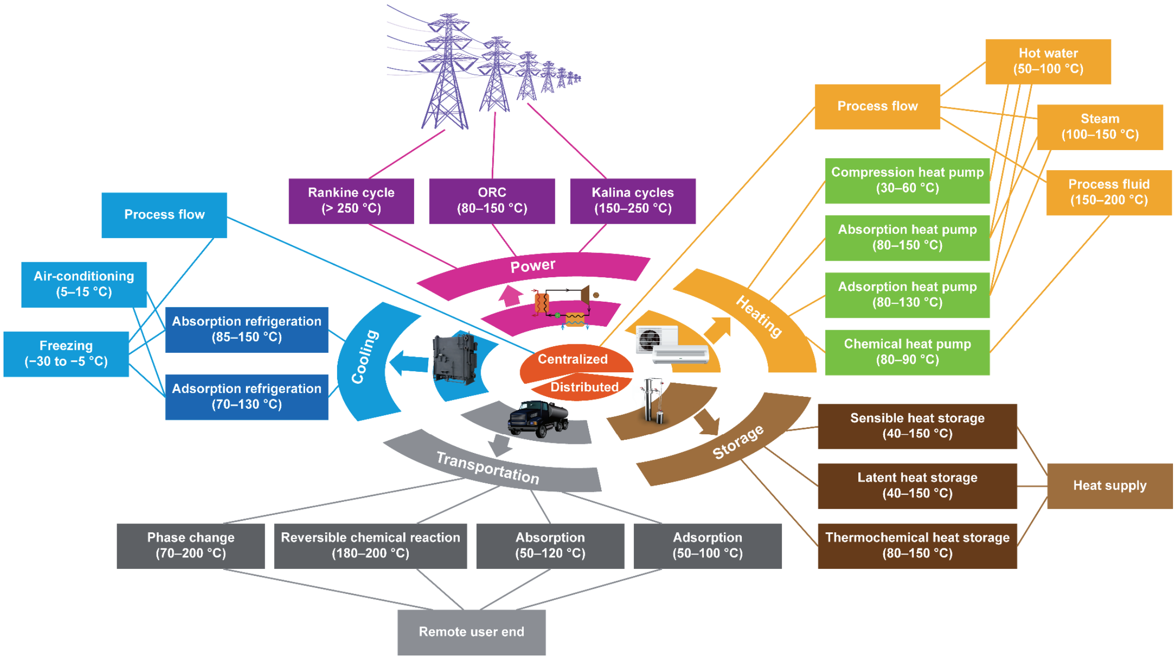

Fig. 21. Network utilization of low grade heat via various energy conversion methods and the integration of centralized and distributed energy systems.

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