

Comprehensive Analysis for State-of-the-Art Adsorption Refrigeration Technologies

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Abstract. With the development of science and technology, society needs more and more energy currently, and the energy utilization efficiency has become a topic that cannot be neglected. In many cases, it is still a common phenomenon in society that a large amount of energy is wasted, which may cause more fossil energy to be burned and the greenhouse effect to be strengthened. In addition to directly improving the utilization rate of energy, we can also reduce energy waste through the recovery and reuse of waste energy. Thermal energy sorption refrigeration technology, divided into adsorption refrigeration technology using solid adsorbent and absorption refrigeration technology using liquid absorbent, could utilize waste energy or low-grade heat sources for refrigeration. Through the introduction of adsorption refrigeration technology, the research and analysis of the application of solid adsorption refrigeration technology in industry, vehicles, ships and buildings, this paper introduces the basic principle and current situation of this technology, summarizes the advantages, disadvantages and development direction of adsorption refrigeration technology, and provides reference for those who do not comprehend this technology or have doubts about the scope of its use.

Keywords: Adsorption refrigeration technologies, Applications, Working principle, Thermal energy.

1. Introduction

As the volume of the world economy increasing, countries have crossed the stage of developing economic scale regardless of any impact, began to care about the impact of their own development on the earth's environment, and increasingly agreed with the concept of green environmental protection. In China, "promoting green development and promoting the harmonious coexistence between man and nature", as well as promoting stable and healthy development, are getting popular as a universal concept.

As global warming intensifies day by day, the impact of the greenhouse effect on all aspects of human life is gradually reflected. The concept of energy conservation and emission reduction is becoming more and more convinced, and the needs of all sectors of society for various emission reduction technologies and energy-saving technologies are also increasing. However, due to the needs of social development, the total energy required for the operation of human society is still increasing. How to effectively improve energy efficiency? The contradiction may make it the primary task under the background of the times. For achieving the purpose of reducing carbon emissions, fully improve the utilization rate of energy and reduce energy waste, the recovery of wasted thermal energy generated in the operation of energy consuming equipment has become an important topic.

As demonstrated in Figure 1, the waste heat recovery technology can be generally divided into section for refrigeration and heating, power, heat exchangers and heat storage. With waste heat recovery technology, the wasted energy in industrial engineering can be recovered and reused, which indirectly saves the combustion of fossil fuels and greenhouse gas emissions, directly improves the industrial thermal efficiency, and is of great help to improve the overall energy utilization rate of the nation.

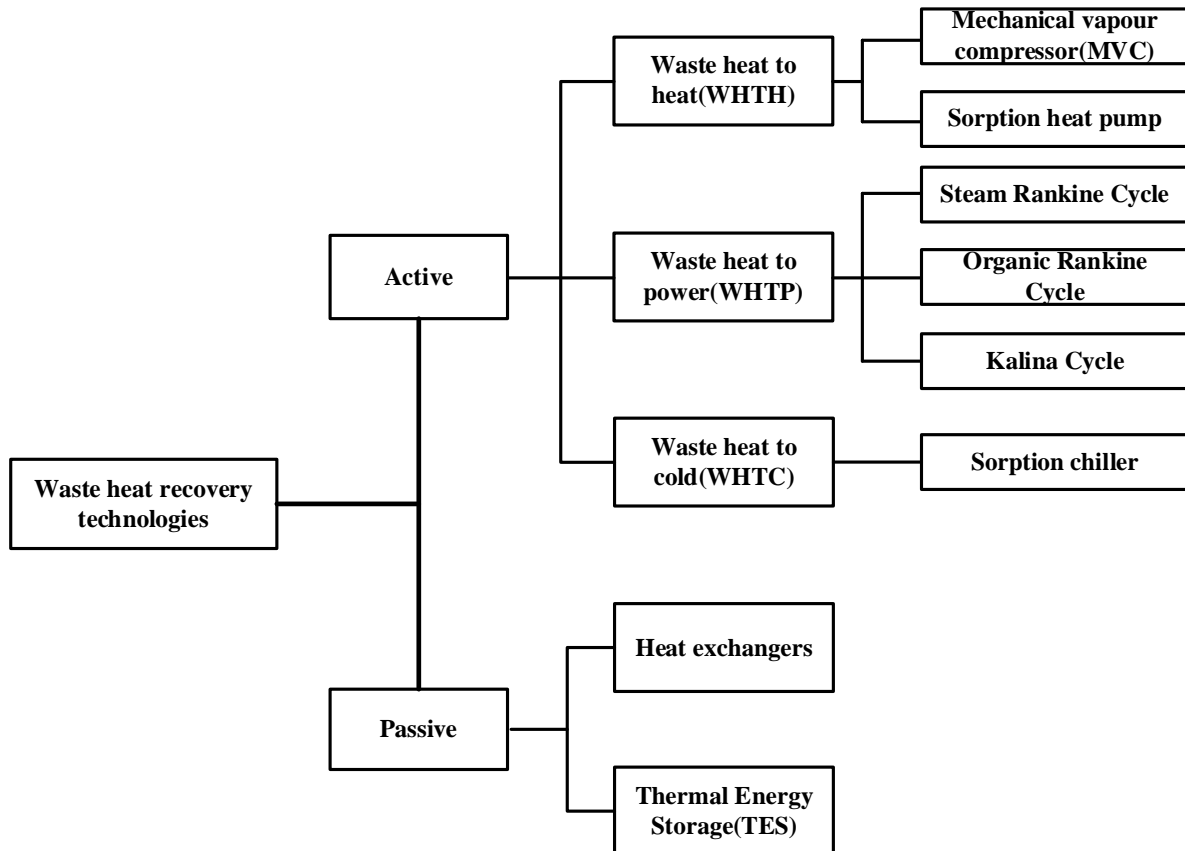


Figure 1. Categorization of waste heat recovery technologies [1]

Waste heat recovery refrigeration technology refers to the technology that recycles the waste heat energy generated in normal scenes and is used for refrigeration. It is a major branch of waste heat recovery technology. In the process of industrial production, energy consuming devices such as metallurgical furnaces and combustion chambers will produce a lot of wasted heat during operation, which is usually discharged in the form of flue gas; In the process of daily life, people often use the combustion of fossil fuels to provide kinetic energy for vehicles such as cars and boats. During the combustion process, a large amount of waste heat is generated. It would be discharged into the air as the tail gas being discharged, or slowly distributed in the air spontaneously. In both cases mentioned above, waste heat recovery refrigeration technology can be used to recover energy. Once replacing the original compression refrigeration air conditioning in factories and transportation vehicles, waste heat recovery refrigeration technology could realize the recycling of heat energy and save the electricity energy use at the same time.

Waste heat refrigeration technology can be divided into absorption refrigeration and adsorption refrigeration. Both two adopt the cycle process of with similar principle. The main difference is the sorbents differ. Absorption refrigeration mostly uses liquids sorbents with good fluidity, such as NH₃-H₂O and lithium bromide; The sorbents of adsorption refrigeration is generally solid medium, such as molecular sieve, calcium chloride, etc. [2] Up to the properties between the sorbents and sorbate, they can be separated when affected by low-grade heat sources and produce high-pressure hot gases. The compressor of the traditional compression refrigeration system is replaced by a structure driven by low-grade heat sources, which replaces the electric energy supply and saves it.

Adsorption refrigeration is of great value for the recovery and reuse of waste heat due to its characteristics of using low-grade thermal energy, stable working conditions and simple structure.

2. Introduction to adsorption refrigeration technology

2.1. Adsorption refrigeration principle

The core principle of adsorption refrigeration is the adsorption of specific refrigerant molecules by solid adsorbents. Adsorption refrigeration mainly includes Adsorption Bed, condenser and evaporator.

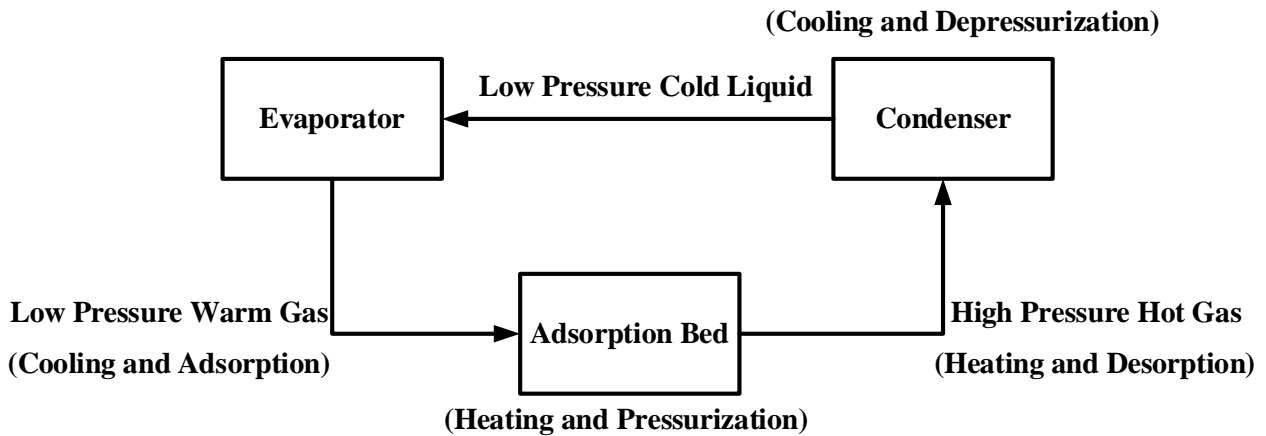


Figure 2. Adsorption refrigeration system

Among them, the adsorption bed, equipped with solid adsorbent, can be driven by low-grade heat energy to desorb refrigerant molecules, then produce high-pressure hot gas. The gas pipeline in the condenser has a large contact area with the air. When the high-pressure hot gas generated from the adsorption bed passes through the condenser, it is converted into low-pressure cold liquid, and then enters the evaporator. The liquid changes back to low-pressure warm gas after heat exchange with the air outside the evaporator. After a series of work, the refrigerant return to the adsorption bed again and being absorbed by the solid adsorbent, completing a thermodynamic cycle (as shown in Figure 2). Figure 3 demonstrated the thermodynamic cycle diagram of the adsorption refrigeration systems.

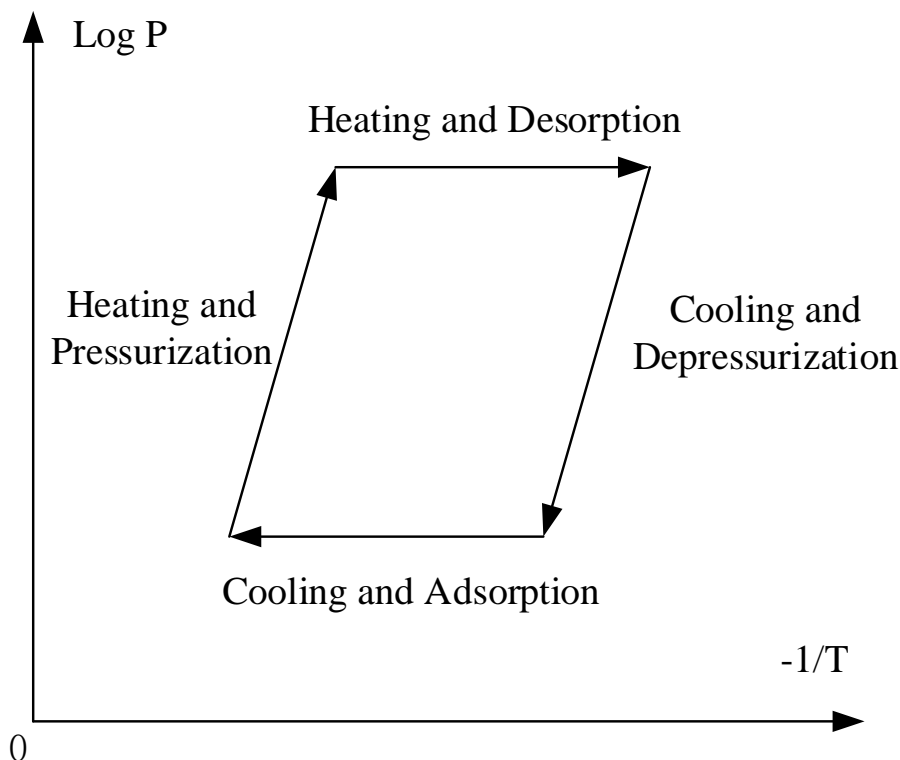


Figure 3. Thermodynamic cycle diagram

2.2. research status

The working capacity of adsorption refrigeration system depends on the working performance of adsorbent and refrigerant, such as the heat absorption and exothermic capacity of refrigerant, the difficulty of liquid solid transformation, etc. The early research on adsorption refrigeration started from the working pairs. The first exploration of absorption and adsorption refrigeration originated in 1848. Faraday found that the process of mercury chloride absorbing ammonia can be used for refrigeration. In the process of studying the performance of working pairs, scientists selected some classical working pairs, such as activated carbon, zeolite molecules, silica gel, calcium chloride, hydride as adsorbents. The refrigerants are mainly represented by methanol, ethanol, ammonia, water, hydrogen, etc.

The early research results made the adsorption refrigeration system proposed. Early physical applications are often used to solve the refrigeration problem in some scenarios. For example, in the early and middle of the 20th century, G.E. Hulse used silica gel sulfur dioxide and calcium chloride ammonia working fluids to refrigerate the food on the train. At the same time, in the process of development and application, it is found that the adsorption refrigeration system based on simple basic cycle has some problems, such as discontinuous refrigeration process, low efficiency, and so on, which need to be improved. The subsequent research work mainly focused on the solution of problems of working pairs, internal system, especially the heat transfer characteristics of the adsorption bed.

In today's research, many researchers' development of adsorption refrigeration system mainly focuses on two aspects: the selection of working pairs that are most suitable for the corresponding working conditions, and the innovative design of the refrigeration system structure.

When selecting working pairs, the first thing to do is to select refrigerants with greater latent heat of vaporization per unit volume and adsorbents with more refrigerant adsorbed per unit volume to improve the efficiency of each refrigeration cycle. Secondly, the higher the sensitivity of the working pairs to heat, the easier the system can be driven, which means expanding the range and total amount of waste heat recovery. Finally, the working pairs should be easy to match the corresponding adsorption bed structure and its materials for achieving stable motion and heat conduction.

Table 1. Feasibility of applying solid adsorption refrigeration to various vehicles

Type	Total power (kW)	Required Refrigerating Capacity (kW)	Available Refrigerating Capacity (kW)
Car	66	2.3	5.0~7.5
Passenger car	84	7~10	6.3~9.5
Bus	150	24	11.3~17.0
Coach	250	15~20	18.8~28.3

When innovatively designing a refrigeration system, its process must be based on a specific working pair. All aspects of the system (materials, structure) should be compatible with the characteristics of the working pair, such as the heat transfer performance of adsorbent and refrigerant, the boiling point of refrigerant, whether the refrigerant is easy to circulate in the structure, etc. Secondly, we should consider whether we can improve the refrigeration COP through some improvement measures on the premise of achieving stable work, such as the structural design of double adsorption beds and multiple adsorption beds, so that multiple adsorption processes can work concurrently, improving the COP. For example, the four-adsorption bed system designed by scientist Jones for activated carbon ammonia working pair can reach an COP of 1.0 when the surrounding

environment temperature is about 35 °. S.G. Wang and others mentioned that using three groups of calcium chloride ammonia adsorption generator system to produce ice from the tail gas heat of fishing boat, the COP reached 0.3, while the fuel consumption increased by only 1.4%.

3. Application scenario

3.1. Industrial application scenarios

Waste heat refers to the heat that primary energy or combustible materials are not used by the process flow after combustion or conversion. According to the temperature, it can be divided into high-temperature waste heat (above 500 °C), medium temperature waste heat (200 ~ 500 °C), and low-temperature waste heat (below 200 °C). According to the different waste heat carriers, waste heat can also be divided into solid carrier waste heat resources, liquid carrier waste heat resources and gas carrier waste heat resources. The waste heat can be converted into mechanical energy Electric energy, thermal energy or cold energy, etc [3]. In China's current industrial industries, examples of waste heat reuse refrigeration are often found in some industries that require a lot of energy consumption, such as oil refineries, steel industries, coking plants, etc. However, most industrial manufacturers prefer absorption refrigeration technology than adsorption refrigeration technology. Most of the working fluids used are TC working fluid or lithium bromide. The reason why large-scale industrial application scenarios choose absorption refrigeration as a means rather than adsorption refrigeration is that absorption refrigeration has achieved large-scale industrial production, with many specifications and relatively mature technology and process. Although adsorption refrigeration was proposed as early as 1929, it has not attracted widespread attention for a long time, signifying many problems to be solved. That's why industrial manufacturers who often pay attention to economic benefits are naturally more willing to choose more mature absorption refrigeration technology.

3.2. Transportation scenario application

3.2.1 Application on Cars

Among all the application scenarios of adsorption refrigeration technology, vehicle has the widest application prospect. Firstly, the thermal efficiency of gasoline and diesel vehicles is low, which means that there is a lot of waste heat resources in the working process of a car to be used. Secondly, as the largest market in the transportation industry, there are many application receptors for adsorption refrigeration system, which might play a huge part in the environment effects.

For household vehicles, the main application for adsorption refrigeration technology is air conditioning refrigeration. Unlike the classic compression refrigeration, adsorption refrigeration does not need a compressor, and is driven by low-grade heat source. However, because of the limit of COP, in practical application, the system structure of double adsorbers is often used to improve the COP of adsorption refrigeration air conditioner. The cop of double adsorption bed is often above 0.2 ~ 0.3, so as to meet the refrigeration needs. Generally, the adsorption refrigeration system with double adsorption beds can make the refrigeration power reach 7.5% - 11.5% of the engine power.

In fact, except for buses, double adsorption bed adsorption refrigeration air conditioners can theoretically meet the needs of conventional refrigeration capacity, as shown in Table 1[4].

The working pair commonly used in conventional car adsorption refrigeration are activated carbon ammonia [5] and activated carbon methanol [6]. The double adsorption bed structures are usually devised. The two adsorption beds are connected in parallel to the same system and work in reverse phase, that is, when one adsorption bed is desorbed, the other adsorption bed is in the adsorption state. When the refrigerant is desorbed from one adsorption bed and condensed into liquid in the condenser, it can immediately enter the other adsorption bed starting adsorption and gasification.

The advantage of the double adsorption bed structure is that the desorption process and the adsorption process occur in two adsorption beds respectively, and there is no need to wait for the heating and cooling process of each adsorption bed. After a working process is completed, the

functions of the two adsorption beds are reversed, and the original desorption adsorption bed is cooled from high temperature. In the process, the adsorption capacity of the adsorbent becomes stronger. As the adsorption generation bed of the new round of working process, the adsorption bed that originally took place gradually heats up, and refrigerant desorption occurs in the process, so as to realize the continuous refrigeration of the whole system, shorten the refrigeration cycle, and improve the refrigeration efficiency.

3.2.2 hull application

The application of adsorption refrigeration technology in ships has always been a hot topic in the application of adsorption refrigeration. The thermal efficiency of diesel generators used in ships is generally only 30% - 40%, and a large amount of waste heat energy can be recycled [7]. At the same time, as the carrier of the fishing industry or transportation industry, the refrigeration capacity required by ships is very huge. At the same time, most of the waste heat of ships belongs to medium temperature waste heat, which is warm enough to drive a variety of working pairs for solid adsorption refrigeration, representing the broad application prospect.

However, the academic research on the solid adsorption refrigeration technology on ships mostly stagnates in the assumption stage at present. There are no successful examples of adsorption refrigeration system for ships yet. For the researchers, there is never a set of design standards, adding many obstacles to the research process [8].

It is undeniable that even if the technology has not yet reached maturity, but the application of adsorption refrigeration in the hull still has its remarkable advantages:

1. The common working medium is non-corrosive to, with long service life and good reliability.
2. Simple structure, stable working process and no noise.
3. Instead of traditional steam compression refrigeration, there is no additional energy consumption, saving navigation costs and fuel resources.

At the same time, the adsorption refrigeration system also has some disadvantages, such as inconvenient maintenance, low energy efficiency ratio, poor heat exchange capacity and so on, due to the use of flue gas for heating, sea water for cooling, and large equipment volume in the marine environment. However, compared with the economic and environmental benefits brought by practical application, the advantages of applying adsorption refrigeration system in ships far outweigh the disadvantages.

3.3. Architectural application scenarios

In the architectural scene, the adsorption refrigeration system is not driven by exhaust gas and waste heat, but by solar energy. Adsorption refrigeration system is often difficult to be applied in various scenes (such as household vehicles) because of its large volume, and there is no such problem when installing adsorption refrigeration on buildings. Compared with adsorption refrigeration installed on movable objects and driven by waste heat and waste heat, the problem of solar powered adsorption refrigeration system in buildings is that the heat supply is not stable enough. It is difficult for the refrigeration system to obtain driving heat energy in the absence of sunshine. The conventional solution is to install an energy storage device between the solar collector and the adsorption refrigeration adsorption bed, so that the uncertain energy input can be stored and transformed into a stable output, so that the refrigeration system can provide relatively stable refrigeration capacity. X.Q. Zhai of Shanghai Jiao Tong university participated in the design of a silica gel hydraulic pair system that can switch and provide refrigeration or heating functions in the presence or absence of a heat storage system. Through research, it is found that although the operation of the non-thermal storage system is less stable than that of the thermal storage system, the non-thermal storage system has higher solar energy collection efficiency and electrical performance coefficient. However, there is no doubt that this adsorption system is feasible. According to the experimental analysis, this system can meet the daily cooling and heating needs, and the investment payback period is within ten years, at least up to two years.

Table 2. Application Scenarios and Comparisons of Different Adsorption Refrigeration Technologies

scene	category	Common working pairs / structures	Advantages /disadvantages	Problems Facing	development direction
Industry	Absorb	TC working medium, lithium bromide	Mature technology, large refrigerating capacity / taking up space, lack of green working pairs	Low cooling efficiency	System volume Cooling efficiency Working pairs' option
vehicle	Adsorb	Activated carbon ammonia, activated carbon methanol/ double adsorption bed	Maintenance convenient, low noise, stable operation / taking up space	Low cooling efficiency Occupied space reducing	System volume Cooling efficiency Working pairs' option
hull	Adsorb	Zeolite molecular sieve water, activated carbon methanol/ multi adsorption bed	Maintenance convenient, low noise, stable operation / low refrigeration efficiency, immature research status	Design standards establishing The seawater corrosion resistance function improving	System volume System durability Working pairs
architecture	Adsorb	Structure of silica gel water/ energy storage system	Overcoming the space factors, sufficient refrigeration capacity / unstable operation without energy storage system	Low cooling efficiency Stable operation ensuring	Cooling efficiency Operation stability

4. Conclusion and Comments

Although the concept of adsorption refrigeration system was put forward early, it has not been paid much attention until recent years. Due to its unique refrigeration principle, adsorption refrigeration, as a refrigeration system with a similar principle to absorption refrigeration, but far from reaching its development maturity, has the advantages that other refrigeration systems cannot fully have, such as many non- corrosive working fluids, very high working stability, simple structure, environment-friendly and still has great potential to be developed.

In the investigation, it is found that the selection of adsorbent refrigerant and the structural design of the system lack clear and perfect design standards. The adsorption refrigeration system mentioned in most papers is developed by individuals for a specific working condition which is lack of universality. And the research of adsorption refrigeration system has rarely been demonstrated in practice, that is, the actual refrigeration system is rarely manufactured, so it is difficult to find more

potential problems. This means that adsorption refrigeration may still have a long way to go from theory to practical large-scale application.

Through the investigation of adsorption refrigeration system in industry, vehicle, hull and architecture, there comes the Table 2.

As shown in Table 2, although adsorption refrigeration technology has the advantages of stable working conditions, green and environmental protection, its own structure is relatively large, and the problems of low efficiency and immature researching status are still important factors that restrict its development.

The large space occupied by the system restricts its use in small equipment (such as household vehicles); Low refrigeration efficiency leads to the need to design more complex structures, which further increases the space volume of the system; The researches' unsystematized, which makes it difficult for large-scale funds to value it, and hinders the possibility of its large-scale application.

However, it is undeniable that adsorption refrigeration still has broad prospects so long as the core issues broken through, namely: 1. Looking for working fluid pairs with better heat exchange capacity and higher efficiency; 2. Higher energy efficiency ratio and system structure matching working fluid pairs; 3. Breaking through the limitation of refrigeration capacity [9]. 4. The reduction of occupied space and its own weight, and the simplification of system structure.

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