Study on Heat Transfer Performance of Phase Change Thermal Storage Heat Pump Water Heater with Carbon Nanotubes

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Abstract. To explore the feasibility of applying carbon nanotubes (CNTs)/paraffin composites to heat pump water heater system, heat transfer characteristics of phase change thermal storage heat pump water heater were analyzed and discussed. It was shown that the melting and solidification rates of nanocomposite were significantly improved upon the addition of CNTs nanoparticles, and the heat pump heat water with thermal storage has good stability in heat storage and release process. There are some differences in the distribution of temperature field in phase change thermal storage system, especially in exothermic stage. Thermal "stagnation" occurs near the corner of the outlet of water medium, so it is necessary to increase the amount of materials appropriately. Compared with traditional regenerative heat pump water heater with water tank, volume of regenerator of heat pump water heater is reduced by about 1/2 with the addition of nano-composites, and the thermal efficiency can reach 86%. The running experimental results of heat pump water heater suggests the reliability of designment of the thermal energy storage and the feasibility of CNTs/paraffin using in the heat pump water heater. The temperature of CNTs-paraffin composites rises faster and the heat transfer time is shorter at higher ambient temperature. Obviously, ambient temperature has a significant impact on the property of heat pump system.

1. Introduction
With the improvement of people’s living standards, the requirements for comfortable hot water are becoming more and more common, and the safety and environmental protection requirements of water heater performance are getting higher and higher [1-2]. In hotels, restaurants, swimming pools and other places, there is a great demand for hot water, but the use of fuel, gas or even coal-fired heating methods has caused huge pollution and damage to the environment and threatened human survival. Therefore, it is very necessary to develop new energy-saving and environmentally friendly domestic water heaters [3-5].

With the rapid development of nano-material science and heat pump technology [6-10], the application of nano-material technology to heat pump systems is of great significance for improving the reliability, economy and miniaturization of heat pump systems, so it is necessary to further increase heat storage density. Since heat capacity of nanocomposite per unit mass is 3 to 4 times that of water, the volume of the nano-phase change heat storage material is 1/3 to 1/4 of hot water storage tank, and greatly reducing the volume of hot water storage tank. If you want to get a higher water temperature without reducing the energy efficiency ratio, it can be achieved by using nano-material
strengthening technology, which reduces the heat transfer temperature difference, and increases the heat transfer coefficient and the energy efficiency ratio. It will improve the overall performance of heat pump water heater with nano-phase change heat storage material. In this paper, CNTs/paraffin nanocomposites are used as phase change thermal storage media, and nanocomposites are used in heat pump water heaters. The effects of carbon nanotube fillers on the heat transfer property of phase change heat pump water heaters are studied.

2. Experimental

2.1. Materials
In the experiment, paraffin was supplied by Shanghai Huashen Recover Equipment Co. Carbon nanotubes (Purity/mass>95wt%, diameter: 10-100 nm, length: 10-30 µm) used in the experiment was supplied by Chengdu Organic Chemicals Co. Ltd.

2.2. Experimental Equipment
The structure diagram of phase change thermal storage heat pump water heater is shown in figure 1. Phase change heat storage tank 4 is equipped with condensation heat exchange coil 8 and water heat exchange coil 9. The output end and the input end of the condensation heat exchange coil 8 are connected with the expansion valve 3, the evaporator 1 and the compressor 7 one by one. A fan 6 is installed at the evaporator 1 and the air flow 2 is blown through the evaporator 1 to exchange heat when the fan 6 works. One end of the water heat exchange coil 9 is connected with a cold water inlet pipe 5, and the other end is connected with a hot water outlet pipe 10. The thermocouples are arranged in the tank 4 and are directly connected to the data collecting instrument 11.

Whole experimental device includes a phase change thermal storage system, a heating system, a water system and a data collecting system [11]. Size of the phase change thermal storage system is 660 mm × 280 mm × 340 mm, and the outside of the thermal storage box is made of polyethylene foam insulation material with a thickness of 20 mm. The heating system uses a small air source heat pump. The flow meter is used to control the flow of inlet water. The data collecting system consists of an Agilent data collecting instrument and the thermocouples. The refrigerant used in the compressor is R22, and the phase change heat storage medium is 0.1 wt% of CNTs-paraffin nanocomposite, and the effective heat is when the outlet water temperature is higher than 40 °C. The ambient temperature and relative humidity are 20 °C and 60% respectively. The arrangement of the thermocouples in the phase change thermal storage device is shown in table 1. Three thermocouples are placed at each place, and the average of the three temperatures is taken as the temperature at the temperature measurement point.

![Figure 1. Structure diagram of phase change thermal storage heat pump water heater.](image-url)
Table 1. The thermocouple arrangement in phase change thermal storage system.

| No. | x (mm) | y (mm) | z (mm) | Description                      |
|-----|--------|--------|--------|----------------------------------|
| 1   | 330    | 140    | 170    | Pipeline next to the refrigerant | |
|     |        |        |        | Inlet and water inlet           |
| 2   | 330    | 210    | 170    | Pipeline next to water outlet    |
| 3   | 330    | 70     | 170    | Corner of device                 |
| 4   | 660    | 280    | 170    | Corner of device                 |
| 5   | 660    | 0      | 170    | Corner of device                 |
| 6   |        |        |        | Hot water outlet                 |

3. Results and Discussion

3.1. Influence of Carbon Nanotube Filler on the Heat Transfer Performance of Phase Change Thermal Storage System

Temperature curves for the phase change process of CNTs/paraffin composites are shown in figure 2, which reflects the temperature distribution of 1, 2 and 3 in the phase change thermal storage device. From the figure, the temperature of the nanocomposite increased rapidly in the early stage of heat storage because of the large temperature difference between nanocomposite and refrigerant. At this time, nanocomposite absorbs heat through sensible heat, and heat transfer was mainly achieved through heat conduction. As the temperature of the nanocomposite is close to the phase change temperature, temperature of the nanocomposite rises very slowly and lasts for a long time, and phase change begins to occur. At this time, heat transfer was mainly achieved through heat conduction and natural convection. Natural convection heat transfer is gradually enhanced, which makes the liquid nanocomposite content gradually increase and the temperature of the nanocomposite rise faster. At this time, the nanocomposite further absorbs heat through sensible heat. From the freezing curve, we can know that the temperature distribution of 1, 2 and 3 are different, which indicates that the heat stored in the nanocomposite transfers the water medium to different degrees, namely the system is efficiently exchanging heat. The heat release process of the nanocomposite is divided into three stages: When the water medium has just entered the phase change thermal storage device, the temperature of nanocomposite decreases very quickly, and at this time the molten nanocomposite releases sensible heat. Then the temperature of the nanocomposite decreases slowly and lasts a long time. At this stage, the nanocomposite slowly releases latent heat. Finally, the temperature of the nanocomposite decreases rapidly, and the nanocomposite releases sensible heat.

Figure 2 also shows that, because the temperature measurement point 1 approaches the refrigerant inlet pipe, the high temperature of the refrigerant and the strong heat transfer capacity of the inlet pipe cause the fastest temperature rise of the temperature measurement point 1. While the temperature measurement points 2 and 3 are far from the pipeline of the refrigerant inlet, so the temperature decreases after the refrigerant flows for a distance, which results in low heat transfer capacity between nanocomposite and refrigerant. During the freezing process, because temperature measurement point 1 is close to the cold water pipe inlet and temperature measurement point 3 is close to the hot water pipe outlet, temperature distribution of 1, 2 and 3 are significantly different. Especially temperature of point 3 is also higher than 40°C at the end of exothermic process. This is because temperature of water medium is a gradual rise of unsteady state during the entire branch flow of the coil. As temperature of the water medium increases, the temperature difference between water medium and nanocomposite gradually decreases, which leads to low heat transfer capacity.
Temperature curves of the temperature measurement points 4 and 5 are shown in figure 3, which reflects the temperature distribution at the corner of the phase change thermal storage device. Figure 3 shows that the change trends of the temperature measurement points 4 and 5 are the same, but there are also differences, especially in the exothermic process. The temperature of the measurement point 4 decreases rapidly, while the temperature of the measurement point 5 keeps at about 50 °C at the end of the exothermic phase, indicating that heat is accumulated near the temperature measurement point 5. So the heat at the corners of the phase change heat storage device is difficult to transfer to the water medium through the heat storage material in a relatively short time, which results in stagnant heat. For practical use, the stagnant heat is an ineffective amount of heat, and it is also a loss of heat from the perspective of thermal energy use.

Based on the above analysis, it is found that there are differences in the temperature distribution in the phase change heat storage system; especially the difference in the exothermic phase is very obvious. There is a slow temperature change phenomenon in some places of the phase change thermal storage device, such as near the corner of the outlet of the water medium, which has little effect on the heat transfer of the entire phase change thermal storage device. When determining the amount of heat storage material, the ineffectiveness of this part of material needs to be considered, and it is necessary to appropriately increase the amount of material [11].

3.2. Hot Water Outlet Temperature Analysis
The ultimate goal of the phase change thermal storage device is to obtain the hot water suitable for domestic or industrial use by heating the water medium. Therefore, the outlet water temperature and
Water output of phase change thermal storage device are one of the important indicators used to evaluate the performance of the energy storage device. It can be seen from Figure 4 that the outlet water temperature drops rapidly first, and then the outlet water temperature drops slowly and lasts a long time due to the phase change of CNTs/paraffin composites, and the outlet water temperature is mainly between 52 °C and 58 °C. Finally, the outlet water temperature drops significantly by releasing sensible heat to the water medium. It can also be seen that the latent heat transfer time of CNTs-paraffin composites is relatively long and the sensible heat transfer time is relatively short during the whole phase change process, which makes the phase change thermal storage system more stable than the traditional heat pump water heater system, indicating that the CNTs-paraffin composites can be used as a thermal storage material for the heat pump water heater.

**Figure 4.** The temperature variation of thermocouple with 6.

Figure 4 shows that the first heat transfer time is 14 minutes and the second heat transfer time is increased to 18 minutes. This is because the heat pump is running at the same time during the second heat transfer. 81 L of hot water can be released during the first heat transfer and 101 L of hot water can be released during the second heat transfer. In practical applications, the outlet water temperature can be adjusted to a suitable temperature by controlling the flow velocity at the inlet of the water medium and the cold water mix. When taking a shower, the shower flow rate is usually 5 L/min, which is 300 L/h. When mixed with the cold water, 81 L hot water is equivalent to a hot water supply of about 128 L water tank. The results show that the heat storage performance of a 62 L phase change thermal storage device is approximately equal to the heat storage performance of a 128 L water storage tank, and the volume of the phase change thermal storage tank is significantly reduced by about 1/2. According to the calculations, the stored heat by CNTs-paraffin composites is 10297 kJ, and the 81 L hot water contains 8845 kJ, and the remaining heat in the phase change thermal storage device is only 1452 kJ, obviously the thermal efficiency can reach 86%. The thermal efficiency of the air source heat pump water heater is lower than 60%, so the thermal efficiency of the phase change thermal storage heat pump water heater is significantly improved, which indicates that the phase change thermal storage system is feasible to replace the water tank of the traditional domestic heat pump water heater.

**4. Conclusion**

In the paper, CNTs/paraffin nanocomposites are used as phase change thermal storage media, and nanocomposites are used in heat pump water heaters. The effects of carbon nanotube fillers on the heat transfer property of phase change heat pump water heaters are studied. Key conclusions can be summarized as follows:

1. With the addition of carbon nanotube fillers, the thermal storage rate and heat release rate of CNTs/paraffin composites are significantly improved. The latent heat transfer time is relatively long, and the sensible heat transfer time is relatively short during the whole phase change process, which
makes the phase change thermal storage system more stable than the traditional heat pump water heater system, indicating that the CNTs-paraffin composites can be used as a thermal storage material for the heat pump water heater.

(2) The addition of carbon nanotube filler makes the heat storage performance of the 62 L phase change thermal storage device equal to the heat storage performance of the 128 L water storage tank, and the volume of the phase change thermal storage tank is significantly reduced by about 1/2. According to the calculations, the stored heat by CNTs-paraffin composites is 10297 kJ, and the 81 L hot water contains 8845 kJ, and the remaining heat in the phase change thermal storage device is only 1452 kJ, obviously the thermal efficiency can reach 86%. The thermal efficiency of the air source heat pump water heater is lower than 60%, so the thermal efficiency of the phase change thermal storage heat pump water heater is significantly improved, which indicates that the phase change thermal storage system is feasible to replace the water tank of the traditional domestic heat pump water heater.

(3) There are differences in the temperature distribution in the phase change heat storage system; especially the difference in the exothermic phase is very obvious. There is a slow temperature change phenomenon in some places of the phase change thermal storage device, such as near the corner of the outlet of the water medium, which has little effect on the heat transfer of the entire phase change thermal storage device. When determining the amount of heat storage material, the ineffectiveness of this part of material needs to be considered, and it is necessary to appropriately increase the amount of material.

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