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Experimental investigation of a novel metal-organic framework (MOF) based humidity pump under high humidity conditions

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Abstract: Latent heat load accounts for a significant proportion of air-conditioning energy consumption and particularly for specific environment in humid climates. Traditional vapor-compression refrigeration dehumidification faces the problem of refrigerant leakage, overcooling and complicated mechanical systems. Here, we report a novel humidity pump that uses semiconductor refrigeration and metal-organic frameworks (MOFs) as dehumidification method, which can efficiently transport moisture from a relatively ‘low-humidity’ space to a high-humidity one. The working principles of the humidity pump were introduced that the process air flows through the cold desiccant coated heat exchanger and then comes into direct contact with the MOF coatings to transfer heat and mass. The dehumidification performance of humidity pump was investigated in high humidity, and the dehumidification coefficient of performance (DCOP), dehumidification rate and moisture removal efficiency using MIL-100(Fe) coatings were calculated. The results indicated that the MOF humidity pump possesses excellent moisture transfer ability.

1. Introduction
With the diminishing of the natural resources, the energy consumption in the building gains much more attention, thus there is an urgent need to search for high-efficient methods for energy utilization [1]. Air-conditioning system as a component of the building systems accounts for a large proportion of total building energy consumption. In the field of indoor hygrothermal control, the solid desiccant dehumidification systems are widely adopted to control the total load, where latent load usually accounts for up to 20-40% [2]. However, this device features increasing temperature at the dehumidification channel due to the inherent adsorption heat of the hygroscopic materials, thus leading to bulky size and low efficiency of the system [3].

To solve these drawbacks, the selection of some novel materials [3] and reasonable design of system framework [4] may be the solution to improve the system performance. As for a conventional desiccant-coated system, the refrigerant inside the tube and the desiccant coating can separately deal with the sensible and latent load of the incoming process air, thus avoiding a large amount of energy consumption. After flowing through the device, the outlet air can be directly vented into the target room. Given these advantages, many have reported the desiccant used dehumidification system [5-7]. However, in these reported systems, the operation performance varies as the employed desiccant changed, and the conventional systems have a series of problems, i.e. the leakage of refrigerant, bulky size, etc. In terms of these problems, some novel materials such as metal-organic framework (MOF) [8, 9] reported with remarkable sorption capacity and gentle regeneration condition can well deal with the poor performance of the traditional materials, and the thermoelectric module (TE) can provide both the cold and hot side for the adsorption and desorption of desiccant without using any refrigerant.
Herein, a MOF-based humidity pump has been prepared to explore its applications in dehumidification. MIL-100(Fe)- a Fe-based MOF material- has been integrated into the device, and the sensitivity analysis has been conducted to investigate the effect of different operation factors (i.e. cycle time, power and air velocity) on the working performance.

2. Methods

2.1. Isotherms
MIL-100(Fe) is synthesized hydrothermally through the combination of Fe$^{3+}$-based metal clusters and trimesic acid, which is prepared as shown in our previous work [9]. Here, the water adsorption characteristics of this MOF were conducted through dynamic vapor sorption (DVS). Figure 1 shows the schematic of DVS, which presents the inner structure of the device. The test sample was put on the sample holder at one side of the microbalance. The built-in-radiant heater provided the isothermal environment (25℃) around the MOF sample, while the vapor pressure was regulated through the mixing of dry and humid N2. In order to maintain the given operation conditions, a designed control panel connected with the temperature and humidity sensor was inserted inside the device to timely regulate the vapor and heat charging flux. 100mg of MIL-100(Fe) was loaded on the sample holder, and then the activation process was performed by vacuum heating 120℃ for 1h. The stepwise pressure change is adopted at each set test point, and the vapor pressure varies from 1Pa to 3000Pa.

![Figure 1. Schematics of dynamic vapor sorption device.](image)

2.2. Humidity pump device
Figure 2 shows the 3D structure of the MOF-based humidity pump. The enclosure is an enclosed acrylic box of 300mm(L) *60mm(W) *130mm(H), and the middle partition plate divided the flow passages into dehumidification side and regeneration side. It can found that the core parts of this device are consisted of two MOF coated heat exchangers and a TE module. In figure 3, two aluminum-based heat sinks with the same size of 100mm(L) *50mm(W) *60mm(H) symmetrically sandwich the TE module. Each heat sink has 11 fins with a 0.132m2 of the total surface area and 0.5mm of coating thickness. The weighed mass of the MOF coated heat sink and the MOF coating are 199.6g and 45g, respectively. The top and bottom sides of the thermoelectric plate are attached to the root of the heat sink, while the other sides are insulated through silicon sealant to reduce thermal loss.

In addition, figure 3 also shows the operation mechanism of this device. According to the thermoelectric effect (Peltier effect), the TE module can provide both heat and cold sides simultaneously, thus avoiding the temperature rise at the dehumidification channel and regenerating the saturated desiccant coatings. The exchange of the dehumidification and regeneration process can easily be achieved by reversing the electric current and switching the flow passages.
2.3 Operation mode

In this paper, Test mode was adopted to the experiments to conduct the sensitivity analysis about the effect of operational factors on working performance. The detailed operation conditions were specified in Table 1. Four digital hygro sensors with accuracy of ±0.2 °C and ±2% RH (SEK-SHTC3-Sensors, Sensirion) were fixed at each inlet and outlet.

| Parameters                          | Values                      |
|-------------------------------------|-----------------------------|
| Indoor air conditions (AD/DE)       | 22.8°C, 60%RH               |
| Cycle time                          | 5min, 10min, 15min          |
| Input power                         | 15W, 20W, 25W               |
| Air velocity                        | 1.5m/s, 3.5m/s, 4.2m/s      |

Figure 2. 3D sketch of the humidity pump.

Figure 3. Schematics of the humidity pump.

Table 1. Operation conditions of Test mode.

Figure 4. Operation mode (Test mode) of the desiccant-coated humidity pump.
As shown in figure 4, the device was put in a temperature and humidity controlled room. The inlet at the dehumidification and regeneration sides was connected directly to the indoor air, which ensures the same inlet air conditions. As the inlet air flows through the surface of the coating layer at the dehumidification side, the water vapor in the air is adsorbed by the desiccant coatings, leading to the decrease in humidity ratio. The cold side of the TE module can deal with the combined heat load, i.e. inherent adsorption heat of the desiccant, convective heat transfer from air and conduction heat from the root of the heat sink. At the same time, the inlet air at the regeneration side flows through the desiccant-coated fins, and brings the released water vapor to the outdoors. Here the hot side of the TE module heats the fins up, leading to the temperature rise at the desiccant coatings and then forming a large vapor pressure gradient between the desiccant and the air. When the desiccant in the dehumidification sides approaches the saturated state, reversing the flow direction of the electric current can switch the position of dehumidification and regeneration. Besides, the switching of the four-way valve at the outlet can guarantee the dehumidified air always from Outlet 1.

3. Results

3.1. Adsorption capacity
The water adsorption capacity of MIL-100(Fe) was investigated through the DVS tests. Figure 5 shows the measured isotherms of MIL-100(Fe) and silica gel (reference) at 298K. It is clear that there is two stepwise increases in the isotherm curves at 0.2P/P0 and 0.4P/P0, respectively, while silica gel gains a sharp increase at a relatively high P/P0 range (>0.6P/P0). This means that MIL-100(Fe) is more hydrophilic than silica gel. In addition, the silica gel has little adsorption capacity (0.09g/g) with <0.6P/P0, but MIL-100(Fe) has strong adsorption capacity in the medium and high P/P0 range (>0.3P/P0).

3.2. Comparison of different desiccants
In order to compare the operation performance using different materials, silica gel is chosen and prepared as the reference group. The basic operation conditions are maintained for these two groups: 1.5m/s of air velocity, 30W of supply power and 20min of cycle time. Figure 6 shows the variation in the humidity ratio difference of outlet air at the top channel. According to the calculation of average humidity ratio difference, the average humidity ratio difference using MIL-100(Fe) can reach 2.33g/kg, while silica gel-based device only has a 1.08g/kg of average humidity ratio difference.
3.3. Operational characteristics

The tentative operation of the device was conducted to observe the variation in the humidity and temperature of the inlet and outlet air. The air velocity here is set at 1.5m/s and the input power is about 30W. 20min of a cycle is adopted in this section.

![Figure 7. Variation of the humidity ratio and temperature at the inlet and outlet air.](image)

Figure 7 shows the measured results of inlet and outlet air conditions at the dehumidification and regeneration sides for two cycles. Within the first half of the cycle (i.e. 0-10min), the humidity ratio in figure 7(a) varies sharply at the first 2min in accord with the temperature change, but then increased (dehumidification side) or decreased (regeneration side) gradually. It can be explained by the sudden vapor pressure difference between the desiccant and the inlet air due to the sudden change in the temperature (switching). The outlet air temperature in figure 7(b) underwent a sharp change in 2min and then gradually flattens. When it switches into the other half cycle (i.e. 10-20min), the functions of the previous channels are interchanged to achieve the successive dehumidification. Besides, from figure 7(b), the temperature rise at the outlet of the dehumidification channel is also observed, which means that the cooling capacity from the cold side of the TE module cannot remove all the accumulated sensible loads under the given operation conditions, but the maximum temperature difference was maintained around 2.7±0.3°C.

4. Discussion

This MOF-based humidity pump can achieve the independent control of temperature and humidity ratio without using a large amount of input power. The utilization of MOF material far outperforms that using traditional materials. To better assess the system performance of the humidity pump, some parameters have been used:

- Dehumidification rate (Ed) indicates the moisture removal within the given cycle time, which is calculated as follows:

\[
E_d = \frac{1}{\Delta t} \int_{t_{ad,s}}^{t_{ad,e}} n_i \ (d_{in} - d_{out}) \, dt
\]

(1)

Where \(n_i\) represents the mass flow rate of the fluid [kg/m³], \(d_{in}\) and \(d_{out}\) are the humidity ratio of inlet and outlet air, respectively. \(t_{ad,s}\) and \(t_{ad,e}\) are the start and end of each dehumidification process.
Moisture removal efficiency ($\eta$) and dehumidification coefficient of performance (DCOP) reflect the power consumption to the corresponding dehumidification rate and the weight of dehumidification capacity to the total power consumption:

$$ \eta = \frac{E_d}{P_{\text{total}}} $$

$$ \text{DCOP} = \frac{\dot{m}_f (h_{\text{in}} - h_{\text{out}})}{P_{\text{total}}} $$

Where $h_{\text{in}}$ and $h_{\text{out}}$ are the enthalpies of the inlet and outlet air at the dehumidification channel. $P_{\text{total}}$ is the total power input for the TE module.

By referring to the detailed operation parameters in Table 1, figure 8 compares the $E_d$, $\eta$ and DCOP of the humidity under different operation conditions. Considering the sorption capacity of the desiccant, figure 8(a) shows that the extension of cycle time at the first stage can increase the amount of the adsorbed water vapor, but when the cycle time is much larger than the time of desiccant to the saturated state, $E_d$ would reversely decrease. $\eta$ is somewhat depend on $E_d$ based on Equation (2), thus the variation of $\eta$ is identical to $E_d$ as the cycle time increases. The variation of DCOP indicates that the best cycle time is around 10min.

In figure 8(b), increasing the supply power can increase the cyclic water uptake of the desiccant, thus
Ed will be increased. It is noted that the increased Ed is limited when the supply power is larger than 20W. In this regard, it can be found that supply power from 15W to 20W can improve $\eta$ and DCOP, but then decrease $\eta$ and DCOP with the supply power increasing from 20W to 25W. Based on Equations (2) and (3), if the moisture removal cannot match with the supply power, $\eta$ and DCOP would be reduced. Figure 8(c) compares the effect of inlet air velocity on the working performance. It is clear that air velocity can affect the efficiency of heat and mass transfer. A larger air velocity can greatly improve the heat transfer coefficient, which can either avoid the accumulated heat at the dehumidification side or weaken the regeneration process at the regeneration side. In this way, Ed and $\eta$ have the same changing trend as the air velocity increases, and here the best air velocity is around 3.5m/s. DCOP will increase along with the increasing air velocity based on Equation (2).

5. Conclusion
The desiccant coated heat exchanger can independently regulate the sensible and latent load but is limited by the selection of desiccant and system framework. In this paper, a MOF-coated humidity pump has been proposed. TE module is used to provide the cold and hot side for the dehumidification and regeneration process, and the MOF material can greatly improve the sorption performance without any corrosion on the metallic heat exchanger. The measured results have indicated that this MOF-based device can efficiently remove the latent load with limited effect on the sensible load. The sensitivity studies demonstrated that the reasonable combination of the operation parameters could give full play to the working performance. The future work will be the measurements of the long-term operation durability, which can estimate the life span of this device and examine its flexibility.

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