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Performance comparison between metal-organic framework (MOFs) and conventional desiccants (silica gel, zeolite) for a novel high temperature cooling system

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Abstract: The use of desiccant-coated heat exchangers (DCHE) in air conditioning systems possesses great advantages in the independent control of both temperature and humidity, as well as low energy consumption and high coefficient of performance (COP). The paper presents a novel high temperature cooling system that uses metal-organic frameworks (MOFs) as sorbents for humidity control. MOFs are a new class of porous crystalline materials consisted of metal clusters and organic linkers, which have an excellent performance of water sorption due to the large specific surface areas and high porosity. In this research, we directly coat MOFs on the heat exchange surface of evaporator and condenser. The evaporator can simultaneously remove both the sensible and latent loads of the incoming air without reducing the temperature below its dew point. The regeneration of wet MOFs is completely driven by the residual heat from the condenser. We also make comparison between the MOF-coated cooling system and conventional desiccants coated ones (i.e. silica gel, zeolite) by way of tests and calculation. The results indicate that the dehumidification capacity of the MOF-coated heat exchanger outperforms other conventional desiccant coated ones under low regeneration temperature (~50°C). The MOF-coated system has a high COP, up to 7.9, and can save 36.1% of the energy required, compared to the traditional vapour compression system with reheating. The amphiphilic MOFs used in the study have high water uptake and low regeneration temperature, and they thus have the potential for being scaled up for large-scale applications in energy efficient air conditioning systems.

Keywords: Humidity control, MOFs, desiccant-coated heat exchanger, energy efficiency

1. Introduction
Electricity demand for heating, ventilation and air conditioning system (HVAC) has gradually been a significant contributor to building energy consumption in the past decades. This because more buildings are supplied with HVAC system to reach desired indoor thermal comfort [1]. Traditional vapor compression system (VCS) generally operated through refrigeration dehumidification process. By cooling the air below dew point, the humidity load is removed by condensation. Such a large temperature difference generally leads to a low COP and even an additional reheating process, and a lower sensible heat ratio like in some hot and humid climates may further worsen the condition [2-3].

Considerable efforts have been made to develop alternative air-conditioning technologies [4-5]. High temperature cooling made possible by novel sorbent or desiccant materials is a promising approach, where a sorption and heat-driven desorption process handles the removal of moisture. Dealing only with the sensible load, the system can raise the evaporation temperature to a higher range, so the COP and energy efficiency of the system can be dramatically improved [6-7].

In view of this advantages, many configurations of dehumidification units coated with conventional sorbent materials were explored [7-9]. However, the working performance of these systems varies greatly for different sorbent materials. Low water uptake ability and high regeneration temperature are the main limitations for the application of conventional sorbents (e.g. silica gel, zeolite etc.) [10].
Metal–organic frameworks (MOFs) are an emerging class of porous materials. Most MOFs can exhibit very high surface areas and large adsorption capacity for gas. Due to their structural and functional tunability, MOFs have become one of the most fascinating classes of materials for both scientists and engineers [11]. Some MOFs with an S-shape isotherm, large water uptake and low regeneration temperature, have been proposed for indoor moisture control [10-12]. With one of the highest water uptake capacity ever reported, MIL-100(Fe) has a better overall performance than other MOFs [10]. We therefore chose MIL-100(Fe) for use in this paper.

In this paper, we first report a new high temperature cooling system integrated with MOF-coated heat exchangers, and secondly, make comparisons between the MOF-coated cooling system and some conventional desiccant-coated systems to investigate their working performance and energy saving potential.

2. Methods
2.1. Adsorption heat exchanger
The main operation component presented here is a fin and tube heat exchanger, in which all the contact surface is coated with MOF including tubes and fins. The MOF-coated heat exchanger can simultaneously process both the sensible and latent load of the incoming air without moisture condensation. There are two working modes as shown in Figure 1(a) and (b). In the adsorption mode, the MOF heat exchanger works as an evaporator, maintaining a low temperature that is slightly higher than the dew point of the incoming air by the cold refrigerant. The hot and humid outdoor air passes through the MOF heat exchanger and is dehumidified and cooled to the conditions required for the supply air by the MOF-coated heat exchanger. This is an isothermal adsorption process. The process continues until the desiccant approaches to its saturation point. In the desorption mode, the MOF heat exchanger acts as a condenser when the sorbent is saturated. The regeneration of the wet MOF coating is completely driven by the heat from condensation of refrigerant. No additional energy is needed. Water vapor previously adsorbed by MOF coating is released and removed by the exhaust air to the outside environment. The MOF coating will be dry and can start a successive dehumidification cycle. Two identical MOF heat exchanger units can ensure the continuous operation of the system by simply reversing the direction of refrigerant and air flow between the two modes.

![Figure 1. Schematics of heat and mass transfer at desiccant-coated heat exchanger (DCHE).](image)

The MIL-100(Fe) used in this paper was synthesized by the École Normale Supérieure in Paris, France (the main partner of this research). The crystalline structure of MIL-100(Fe) has a rigid three-dimensional cubic form, composed of oxo-centered iron (III) octahedral trimers linked to trimesate
ligands \( \text{[Fe}_3\text{O(H}_2\text{O)}_2\text{(OH)(BTC)}_2] \), creating two mesoporous cavities of 25 and 29Å. The SEM image is shown in Figure 2. The tiny crystal of MIL-100(Fe) is octahedral with the size of 0.5–2 µm. This polymer desiccant, an archetypal amphiphilic MOF, exhibits a distinct water capacity owing to its high porosity, typically showing a sigmoidal curve at middle \( p/p_0 \). These properties create the condition of using low regeneration temperature (lower than 50°C).

![Figure 2. SEM image of MIL-100(Fe).](image)

![Figure 3. Water adsorption isotherms of different desiccant at 298K.](image)

From Figure 3, it can be seen that MIL-100(Fe) has barely ability to adsorb water vapor (below 20%) and its water uptake capacity between a typical relative range (20% for desorption phase and 80% for adsorption phase) is 0.46g/g, which is much higher than other conventional desiccants. In addition, the coating procedures, using a water-borne binder of silica sol, enable MOF layer to retain its water sorption features and capacity. The final configuration of DCHE and schematics of heat and mass transfer are presented in Figure 1(c) and (d), respectively.

2.2. Experimental setup

The experimental setup consists of a traditional vapor compression system with DCHE that can effectively control outlet temperature and humidity, as shown in Fig.1(c). In order to achieve a continuous operation, two of the same DCHEs will take turns as condenser and evaporator. The configuration of heat exchanger (20cm×5cm×15cm) consists of 0.2 mm-thick aluminum fins and 7.5 mm-diameter copper tubes. Fin spacing 1.7 mm, fin volume 120 mm × 25 mm × 125 mm = 0.37 L, total dimension 150 mm × 25 mm × 150 mm = 0.56 L, the total mass 225 g. The coating thickness is less than 1mm with 85.6g MIL-100(Fe) being coated on the surface of fins and tubes.

2.3. Test procedure

The experiments aim to explore the regulation of latent and sensible load during adsorption/desorption cycle by measuring air and desiccant operational parameters. Temperature and humidity sensors were installed both upstream and downstream of the heat exchanger in the air duct. During adsorption test, the MOF starts in dry condition. The ambient air at a certain temperature and humidity (30°C, 50% RH) passes through the evaporator, and is dehumidified by MOF coating and cooled by the cold refrigerant. In this phase, the adsorption tests can operate at a desired temperature and avoid the influence of adsorption heat. When the water uptake of MOF coating reaches 0.4g/g, the adsorption test finishes. Then the refrigerant (water) flow was switched oppositely from cold flow to hot flow to achieve the regeneration of the saturated MOF. Air humidity ratio and temperature out of evaporator and condenser are continuously measured and logged.
3. Results and discussion

Given the set outdoor air condition, two baselines with uncoated heat exchanger were used in comparison with MOF-coated heat exchanger as shown in Figure 4a: Air process 1, traditional high temperature cooling without dehumidification; Air process 2, traditional vapor compression cooling with refrigeration-based dehumidification (evaporation temperature generally less than 7~9°C). Air process 3, traditional high temperature cooling with MOF-coated heat exchanger. When the evaporation temperature was set to 19°C, slightly above the dew point, the MOF-coated heat exchanger in Air process 3 cut the humidity ratio of air from 13.6g/kg to 8.5g/kg within its operation time. The adsorption operation continues around 10min, with a maximum humidity ratio change value of 10.6g/kg. The regeneration runs at three different regeneration temperature (40°C, 45°C, 50°C). Fig. 4b shows that the maximum exhaust air humidity ratio at 50°C is twice higher than that of 40°C of regeneration temperature, which means the system can operate efficiently even though the regeneration is powered by a very low-grade heat source (around 50°C). With the present concept, the waste heat from the condenser with a temperature lower than 50 °C can be used for moisture desorption. We estimated that the present system can reach a high COP of 7.9 on a typical summer day in an oceanic climate (e.g. Europe) while maintaining high specific cooling power (SCP).

![Figure 4. The air humidity change during adsorption and desorption process.](image)

Besides, the test results presented in Figure 5 indicate that the supply air of Air process 1 (21°C, 87%RH) is extremely humid and outside the indoor comfort zone, and supply air of Air process 2 (12°C, 95%RH) may cause vapour condensation in the indoor environment, which promote microbial growth and deteriorate the indoor air quality. To reach the same state of supply air as Air process 3, there should be some extra reheating energy in traditional vapor compression system in Air process 2 (Figure 5). When giving the same test conditions, it can be seen that MOF-coated cooling system can eliminates up to 36.1% of working load in conventional vapor compression system with reheating shown in Figure 6. This means desiccant-coated system can avoid the problems of cooling below dew point.

Theoretically, the integration of desiccant-coated component in traditional cooling system to independently regulate the sensible and latent load gives the possibility to make full use of low-grade energy. The low-temperature heat source for desiccant regeneration (~50°C) is well compatible with the original system. Considering the advantages of desiccant-coated cooling system, some conventional desiccant (i.e. silica gel and zeolite) were also applied and measured in comparison with this MOF-coated cooling system. Thus, we have firstly measured the cyclic water uptake of different desiccant under different temperature pair (evaporation temperature-condensation temperature: 20°C-45°C and 20°C-50°C). Table 1 shows that the cyclic uptake of MIL-100(Fe) is about 0.56kg/kg dry mass with 30°C, 50% of outdoor air condition, which means it has a low water uptake capacity at a relatively high
temperature and can make the use of low-temperature heat source possible. In addition, it is clear to see that the dehumidification capacity of MIL-100(Fe) is 5 times as that of zeolite below 50°C, so zeolite can barely achieve regeneration under low temperature heat source.

![Figure 5. Psychrometric comparison of different air process.](image)

**Figure 5.** Psychrometric comparison of different air process.

![Figure 6. Comparison of energy consumption for different air processes](image)

**Figure 6.** Comparison of energy consumption for different air processes

<table>
<thead>
<tr>
<th>Regeneration temperature</th>
<th>MIL-100(Fe)</th>
<th>Silica gel</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°C</td>
<td>0.56</td>
<td>0.23</td>
<td>0.09</td>
</tr>
<tr>
<td>50°C</td>
<td>0.54</td>
<td>0.24</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Table 1.** Cyclical water uptake of different desiccant with 20°C of evaporation temperature.

<table>
<thead>
<tr>
<th>Average supply air</th>
<th>MIL-100(Fe)</th>
<th>Silica gel</th>
<th>Zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>21°C</td>
<td>8.5g/kg</td>
<td>11.1g/kg</td>
<td>12.4g/kg</td>
</tr>
<tr>
<td></td>
<td>(55%)</td>
<td>(71%)</td>
<td>(79%)</td>
</tr>
</tbody>
</table>

**Table 2.** Outlet air condition under same temperature pair (20°C-50°C).

In view of the adsorption characteristics for these desiccants, there is a comparison presented in Table 2 made to investigate the effect of different desiccant-coated systems with the same sensible load and outdoor air condition (30°C, 50%). It is clear that MOF-coated cooling system can reach the comfort zone, while the silica gel and zeolite cannot achieve it. Compared with Air process 1 above, low temperature can barely help zeolite achieve regeneration. Some recent researches [7, 9] try to use silica gel supported salt desiccant, but the direct contact with metal heat exchange will lead to its corrosion and worsen operation performance. Thus, the proposed system is very competitive with most commercial cooling systems.

**4. Conclusions**

The MOF coated heat exchanger can achieve a good performance in removing both latent and sensible heat loads simultaneously for a novel high temperature cooling system. The experimental prototype can operate with a cyclical loading difference of 0.56kg/kg dry mass. During a quasi-isothermal adsorption process, the MOF-coated system reduces about 36.1% of the working load in traditional vapor
compression system with reheating. In addition, given the same evaporation and regeneration temperature, the cyclical water uptake of MIL-100(Fe) distinctly outperforms other traditional desiccants (i.e. silica gel, zeolite), which means a strong ability to regulate the humidity load with less operation time and regeneration energy. We also make a comparison among different desiccant coated cooling systems, and the results prove that MIL-100(Fe) is a promising alternative to conventional desiccants with less regeneration energy source.

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Reference