Research Article

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Energy storage analysis of R125 in UIO-66 and MOF-5 nanoparticles: A molecular simulation study

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Abstract: The efficiency of thermodynamic cycles can be improved by using the optimized working fluid. In the present paper, classic molecular dynamics simulations and grand canonical Monte Carlo were employed to examine the thermal energy storage characteristics of R125/UIO-66 and R125/MOF-5 nanofluids. The results indicate that the adsorption of R125 in MOF-5 is larger than that in UIO-66. Also, the thermal energy storage capacity of R125 was strengthened by mixing with UIO-66 or MOF-5 nanoparticles. In addition, the R125/UIO-66 mixtures can store less energy than that of R125/MOF-5 mixtures except the temperature difference is 30 K to 50 K.

Keywords: R125; UIO-66; MOF-5; thermal energy storage; molecular simulation.

Nomenclature

Δh_{MOHCs}	The enthalpy difference of MOHCs (kJ/kg)
Δh_{Fluid}	The enthalpy difference of pure working fluid (kJ/kg)
$\Delta h_{\text{desorption}}$	The enthalpy difference of desorption (kJ/kg)
T	Temperature (K)
C_p	The heat capacity of MOFs particles (kJ/(kg·K))
a	The mass fraction of MOFs in MOHCs (%)
M	Adsorption (mmol/g)
P	Pressure (kPa)

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1 Introduction

The energy crisis and environmental issues have become the prominent problems in the fast development of our society. Improving the efficiency of energy resource utilization has become one of the popular approaches of sustainable development [1]. The working fluid serves as the heat-carrier of the thermodynamics cycles which are the important way of energy conversion. Thus, using methods to improve the thermophysical properties of the working fluid can optimize the energy efficiency [2].

Actually, extensive research [3] reported that adding nanoparticles to working fluid will modify the heat and mass transfer properties of the working fluid [4-6]. In addition, the unique energy storage mechanism has been explored [7]. For instance, the carbon nanotube, metal-organic frameworks (MOFs) and zeolites are the classical micro/nanoporous materials which have been widely used in industry. Compared to the conventional materials with relative low specific surface area, these materials have a very great specific surface area. The fluid molecules are readily adsorbed on the materials' surface [8]. Since the desorption of fluid from a surface is endothermic, the thermal energy can be stored in the nanofluid by fluid molecules adsorbing and desorbing to materials' surface [9]. Elsayed et al. [10] experimental studied the characteristics of CPO-27(Ni)MOF and proved its feasibility of energy storage. Rezk et al. [11] studied the ethanol adsorption properties in six kinds of MOFs. Chen et al. [12] studied the energy storage of nanofluids containing carbon nanotube under the fields including heat, force and electric coupling actions. McGrail et al. [13] at Pacific Northwest National Laboratory of US proposed to add the MOFs nanoparticles to refrigerants to form the so-called metal-organic heat carrier nanofluids (MOHCs) to enhance the performance of organic Rankine cycle (ORC). Recently, Zheng et al. firstly reported the adsorption isotherms of R134a in Ni-MOF-74 by experiments [14]. The MOHCs need further research for their great potential applications in the utilization of low grade energy and refrigerating cycles.

MOFs are organic-inorganic hybrid material [15], made of metal clusters (or metal ions) and organic ligands via the coordination bond. With great properties of high specific surface area, good thermal stability and strong adsorption affinity, MOFs have a great prospective in the fields of materials, energy and chemistry and so on [16].

However, due to the pores of MOFs being small, it is still difficult to use conventional experimental and theoretical methods to explore the characteristics of MOFs. Recently, with the developing of computational technology, which is not restricted by the experimental conditions, molecular simulation [17,18] can reveal the micromechanism of the macro phenomenon. As a result, it has been widely used in the designing and researching materials. A large number of articles in literature [19] show that molecular simulation has become a powerful tool in studying nanomaterials. UIO-66 [20] is one of the MOFs, containing Zr, developed by the University of Oslo in Norway in 2008. The material is made up of Zr's positive eight-hedral and 12 organic ligands to the two formic acids, forming a three-dimensional skeleton with a central hole cage having eight sides and eight tetrahedral cages, which is one of the most stable MOFs. MOF-5 [21] is a kind of MOFs and consists of clusters (Zn₄O) connected by the 1,4-benzodicarboxylate ligands. It owns good thermostability whose structure remains stable below 573 K and a specific surface area of 2000 m²/g [22].

Pentafluoroethane (R125 [23]) is a common organic refrigerant with low GWP (Global Warming Potential), zero ODP (Ozone Depletion Potential) and good thermophysical properties. Consequently, here, thermal energy storage properties of R125 in UIO-66 and MOF-5 nanoparticles are analyzed by using molecular simulations.

2 Models and simulation details

Notionally, the thermal energy storage properties of MOHCs (Δh_{MOHCs}) is primarily composed of [24]: a) Enthalpy difference of pure working fluid (Δh_{Fluid}) at different temperature b) Thermodynamic energy difference of MOFs particles ($(\int_{T_0}^T C_p dT)_{\text{MOFs}}$) at different temperature c) Desorption heat of working fluid in MOFs ($\Delta h_{\text{desorption}}$) at different temperature, which can be calculated by [25]

$$\Delta h_{\text{MOHCs}} = (1-a) \cdot \Delta h_{\text{Fluid}} + a \cdot \Delta h_{\text{desorption}} + a \cdot \left(\int_{T_0}^T C_p dT \right)_{\text{MOFs}} \quad (1)$$

where a is the mass fraction of nanoparticles in MOHCs. And it could be rewritten as follow,

Figure 1: 2×2×2 unit cells of UIO-66 structure.

Figure 2: 2×2×2 unit cells of MOF-5 structure.

$$\Delta h_{\text{MOHCs}} = \Delta h_{\text{Fluid}} + a \cdot (\Delta h_{\text{desorption}} + \left(\int_{T_0}^T C_p dT \right)_{\text{MOFs}} - \Delta h_{\text{Fluid}}) \quad (2)$$

Thus, more thermal energy can be stored in MOHCs than the pure working fluid while the sum of thermodynamic energy difference of MOFs and desorption heat of working fluid in MOFs is great than the enthalpy difference of the pure fluid.

To compute the value of Δh_{MOHCs} , Δh_{Fluid} could be easily acquired by experiments or simple thermodynamic calculations. Therefore, the thermodynamic parameters of R125 are searched from the National Institute of Standards and Technology (NIST [26]). As a novel material, the C_p of MOFs is rarely reported, and that could be computed through classic molecular dynamics (MD) by analyzing the energy change curves during heating [27]. The $\Delta h_{\text{desorption}}$ could be calculated by Grand Canonical Monte Carlo (GCMC) simulations [28].

Figure 3: Molecular structure of R125.

2.1 Models of simulation

The computational model of the UIO-66 particle is composed of 8 ($2 \times 2 \times 2$ in $X \times Y \times Z$) unit cells of UIO-66, as presented in Figure 1. The system contains 3648 atoms (including 1536 C, 896 H, 1024 O, and 192 Zr). The computational model of MOF-5 particle is also comprised of 8 ($2 \times 2 \times 2$ in $X \times Y \times Z$) unit cells, as presented in Figure 2, made of 256 Zn atoms, 1536 carbon atoms, 832 oxygen atoms and 768 hydrogen atoms. And the molecular structure of R125 (CF_3CHF_2) is presented in Figure 3.

The classic MD and GCMC simulations are using Materials Studio [29]. In the present work, the intra and inter molecular interactions were calculated by COMPASS [30] force field. The long-range Coulombic interactions were described by the Ewald method. Besides, periodic boundary conditions (PBC) are used in all dimensions in the simulations.

2.2 Details of classic MD

The classic MD were simulated in the Forcite component of Materials Studio software. The timestep is chosen as 0.01 fs. The total equilibrium time is 200 ps to compute the different thermodynamic energies of UIO-66 and MOF-5 models at 280 K, 300 K, 320 K, 340 K, 360 K, 380 K, 400 K and 420 K, respectively. The simulations are computed in NVT canonical ensemble with Berendsen algorithm to maintain the temperature.

2.3 Details of GCMC

The GCMC computations were simulated in the Sorption component of Materials Studio software. And the adsorption isotherms at the same temperatures in MD

Figure 4: The adsorption isotherms of R125 adsorb in UIO-66 structure.

Figure 5: The adsorption isotherms of R125 adsorb in MOF-5 structure.

simulations of R125 in UIO-66 and MOF-5 models are computed from 1 to 8,000 kPa. In addition, the Peng-Robinson equation is used to calculate fugacity. For every data of the adsorption isotherms, the equilibrium time is 50,000 cycles with another 100,000 cycles for statistic.

Ethical approval: The conducted research is not related to either human or animal use.

3 Simulation results and Discussion

3.1 Adsorption isotherms

The adsorption isotherms of R125 in UIO-66 and MOF-5 models are plotted in Figure 4 and Figure 5, respectively. The calculated adsorption isotherms decrease as the temperature rises. Naturally, the fluid molecules have

Figure 6: Thermodynamic energies of MOF-5 and UIO-66 particles at different temperature.

Figure 7: The enthalpy difference at different temperature difference (5 MPa).

Figure 8: The relative energy change of working fluids at different temperature difference (5 MPa).

more kinetic energy as the temperature increases. This will result in the decreasing of adsorption for more fluid molecules in overcoming the attractive force from the MOFs. Also, the adsorption capacities of R125 in both UIO-66 and MOF-5 increase as the pressure increases. The adsorption capacity keeps stable until the system reaches its saturation state. Note that the MOF-5 nanoparticle adsorb more R125 than that of UIO-66. This is because the pore size of MOF-5 is larger than that of UIO-66 [14,31].

3.2 Thermal energy storage

The thermodynamic energies of MOF-5 and UIO-66 structures are shown in Figure 6, respectively. Thermodynamically, the increment of thermodynamic energies curve at different temperature is the heat capacity, C_p , of the studied material. Here, the C_p of UIO-66 is about 1.744 (kJ/kg•K), while the C_p of MOF-5 is about 1.878 (kJ/kg•K). The difference of heat capacities of UIO-66 and MOF-5 between the simulation results and the reported data [32] is expected to be the result of the different structures and components of MOFs materials.

Then, the thermal energy storage capacity of the studied UIO-66/R125 and MOF-5/R125 MOHCs could be computed based on eq.(2). The thermodynamic energy difference of studied nanoparticles, desorption heat of working fluid in MOFs and the enthalpy difference of pure working fluid R125 are presented in Figure 7. It should be noted the temperature of cold source is assumed as 280 K. And the thermal energy storage characteristics of the studied UIO-66/R125 and MOF-5/R125 MOHCs with different mass ratio of UIO-66 and MOF-5 nanoparticles are shown in Figure 8. The enthalpy difference of pure R125 is considered as the reference working fluid. The results denoted that the R125/UIO-66 and R125/MOF-5 MOHCs can store more thermal energy than the pure R125. This is because that the thermodynamic energy difference of UIO-66 and MOF-5 are much larger than the enthalpy difference of pure R125 as shown in Figure 7. And the thermal energy storage ratio of the studied MOHCs enhance as the mass fraction of MOFs nanoparticle increased. This is in line with the reported results [14,21,32]. Here, the energy storage capacity of the studied MOHCs is enhanced when the temperature difference is less than 80 K.

In addition, the R125/MOF-5 MOHCs can store more energy than that of R125/UIO-66 MOHCs except when the temperature difference is 30 K to 50 K. The reason is that the desorption heat of R125 in UIO-66 structures is larger than that of R125 in MOF-5 structures when the temperature difference is 30 K to 50 K, even though the

thermodynamic energy difference of MOF-5 particle is larger than that of UiO-66 particle.

4 Conclusions

In the present research, two molecular simulation methods, including classic MD and GCMC, are used to study the thermal energy storage characteristics by the adsorption of R125 in UiO-66 and MOF-5 nanoparticles. The MOF-5 absorbs more R125 than UiO-66 because the pore of MOF-5 is larger than that of UiO-66. Both R125/UiO-66 and R125/MOF-5 MOHCs can enhance the thermal energy storage properties of R125. And the energy storage properties of R125/UiO-66 and R125/MOF-5 MOHCs perform to different abilities due to the difference of thermodynamic changes of MOFs nanoparticles and desorption heat.

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Appendix

Table 1: Thermodynamic Energies of MOF-5 and UIO-66.

Temperature (K)	MOF-5 (kJ/kg)	UIO-66 (kJ/kg)
280	-6340.637628	-28833.57371
300	-6303.646033	-28798.27956
320	-6267.476843	-28764.29193
340	-6229.649899	-28728.52663
360	-6193.184919	-28692.75755
380	-6154.050674	-28659.42097
400	-6115.595878	-28624.21363
420	-6077.80793	-28589.42334