Supporting information

High-throughput computational screening on potential adsorbents

for thermal compression CO$_2$ Brayton cycle

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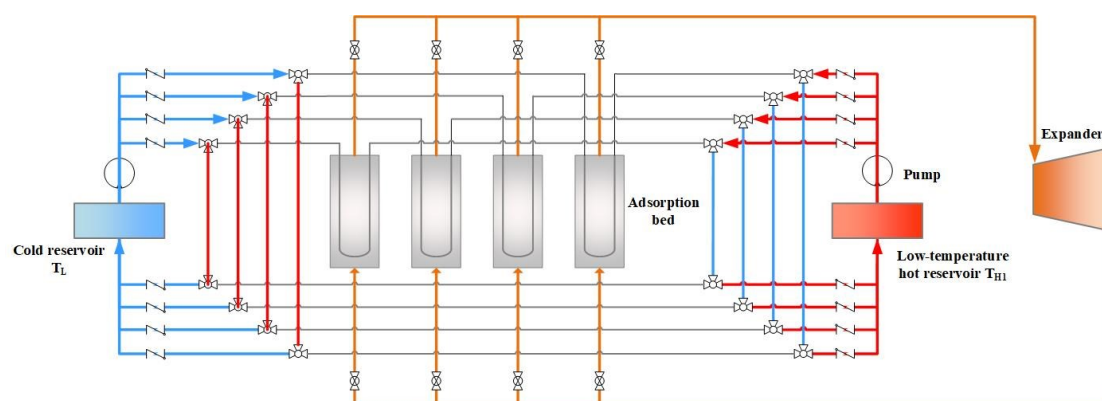
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S1. Detailed Description of CO$_2$ thermal Brayton cycle

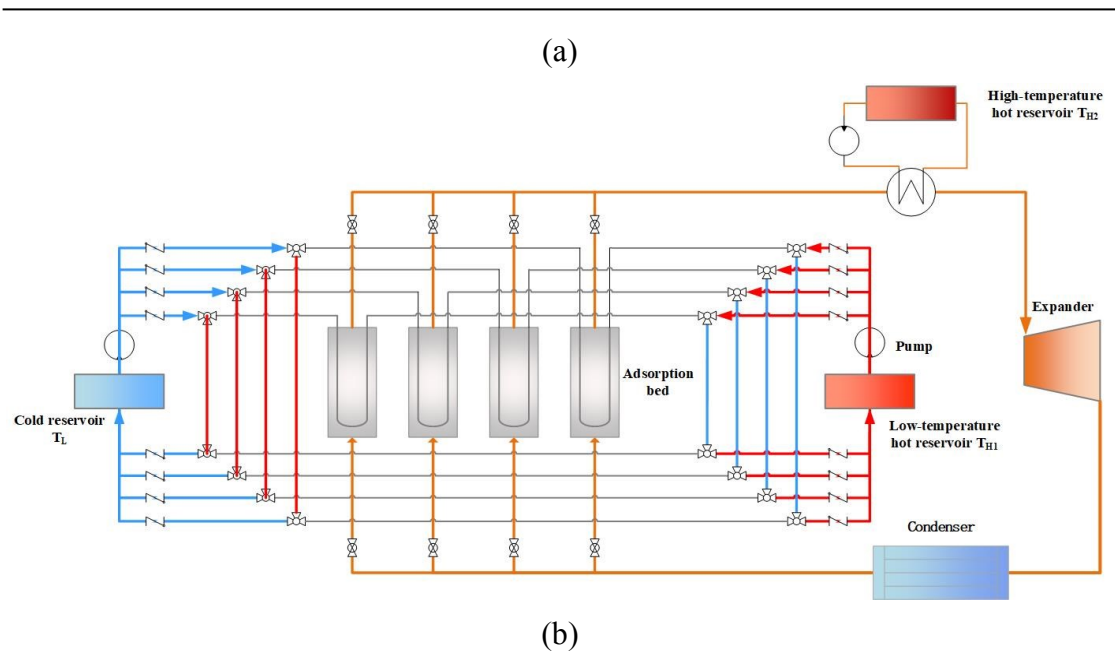S1.1. Diagrams for CO$_2$ thermal Brayton cycle

(b)

Figure S1. Schematic arrangement of the TC-CBC with the high-temperature heat source. Orange lines: power cycle loop; others: adsorption-driven compression loop.
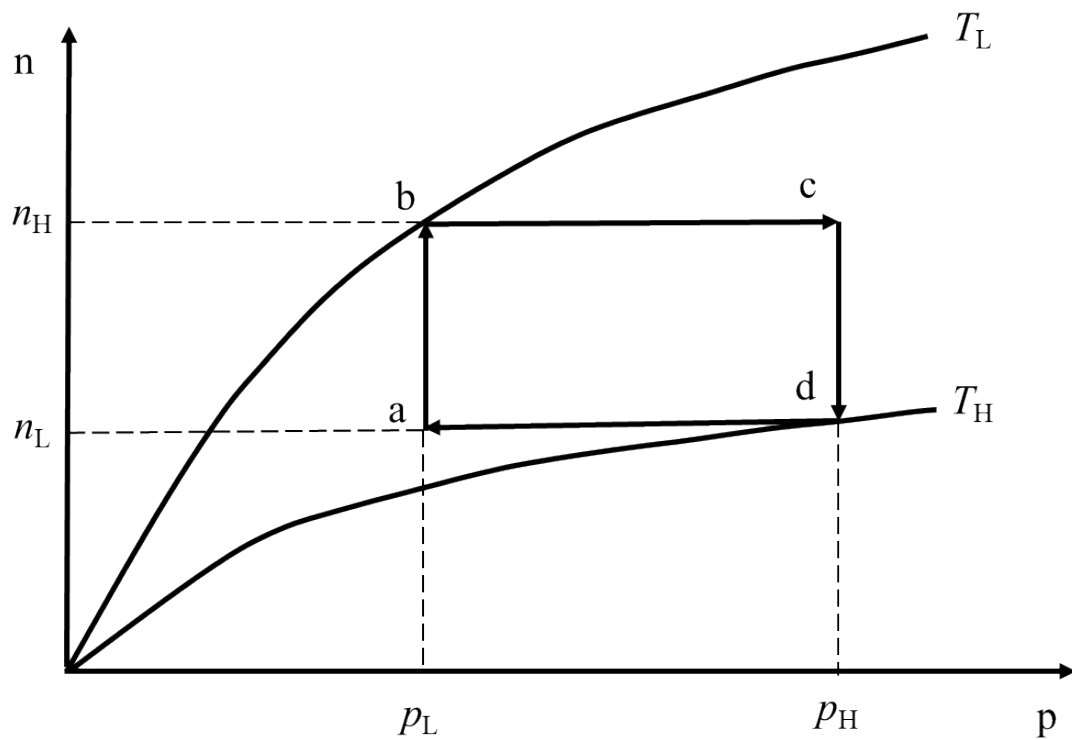

Figure S2. Loading-pressure diagram of adsorption loop consisting of four steps: a-b: Cooling and adsorption; b-c: heating and pressurization; c-d:heating and desorption; d-a:cooling and depressurization.
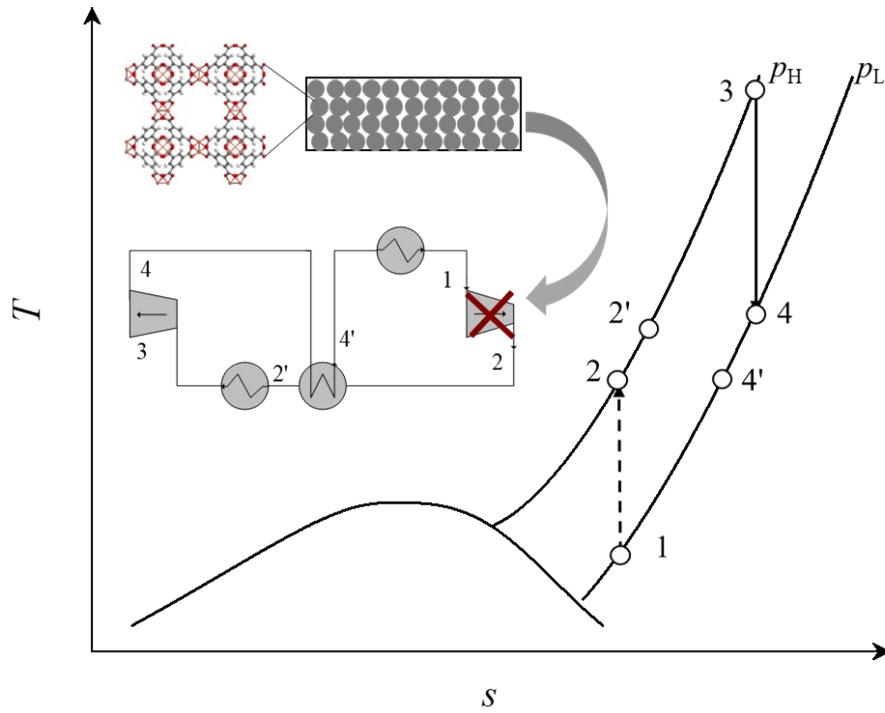
Figure S3. *T-s* diagram for the TC-CBC with heat recovery.

S1.2. Derivation of thermodynamic indicators

As shown in Fig. 2, the specific work output is:

$$w = h_3 - h_4 \qquad \text{\\* MERGEFORMAT (S1)}$$

For a given power generation of P, the working fluid flow is:

$$m_{CO_2} = P/w \qquad \text{\\* MERGEFORMAT (S2)}$$

One of the significant differences between the adsorption-driven compressor and mechanical compressor is that the cycle time of the former is much longer [1]. Adsorption/desorption times τ were chosen as 600 s in this work. Thus, the amount of working fluid which the compression unit has to adsorb is:

$$M_{CO_2} = m_{CO_2}\tau \qquad \text{\\* MERGEFORMAT (S3)}$$

For an adsorbent with a working capacity of WC_{CO_2}, the adsorbent needs to be filled in

the bed is:

$$M_{adsobent} = M_{CO_2} / WC_{CO_2} \qquad \backslash* \text{ MERGEFORMAT (S4)}$$

Thus, the work output per unit mass of adsorbent is:

$$w_{adsorbent} = \frac{wM_{CO_2}}{M_{adsorbent}} = (h_3 - h_4)WC_{CO_2} \backslash* \quad \text{MERGEFORMAT}$$

(S5)

For the TC-CBC with a high-temperature heat source, the total energy consumption (Q_{in}) is composed of energy used to compress the working fluid in the thermal compression unit (Q_{re}) and energy needed to heat the working fluid further in a high-temperature heat exchanger (Q_{heat}).

Using low-temperature heat sources, the adsorption bed is heated to realize the compression and desorption. Energy consumption of this process is commonly dependent on three main contributions: 1) the enthalpy difference of working fluid from point 1 (p_L, T_1) to point 2 (p_H, T_2) in Fig. 1 (Q_{CO_2}); 2) sensible heat of adsorbent material from a temperature of T_1 to a temperature of T_2 (Q_{cap}); 3) and latent heat of desorption (Q_{ads})：

$$Q_{re} = Q_{CO_2} + Q_{cap} + Q_{ads} = M_{CO_2} \times (h_2 - h_1) + C_p \times (T_2 - T_1) + Q_{ads} \backslash*$$

MERGEFORMAT (S6)

where C_p is the heat capacity of the adsorbent, while Q_{ads} can be calculated as followed:

$$Q_{ads} = \int_0^{q_{ad}} q_{st} dq - \int_0^{q_{de}} q_{st} dq \qquad \backslash* \text{ MERGEFORMAT (S7)}$$

Apart from the energy consumption for thermal compression unit, the energy consumed to heat the working fluid further by the high-temperature heat source is (Q_{heat}):

$$Q_{heat} = M_{CO_2} \times (h_3 - h_2) / M_{adsorbent} \backslash* \text{ MERGEFORMAT (S8)}$$

Then, the total input energy is (Q_{in}):

$$Q_{in} = Q_{re} + Q_{heat} \qquad \text{* MERGEFORMAT (S9)}$$

If the high-temperature heat source is not considered, the process 3-4 and the process 1-2 on T-s plane will overlap in Fig. 2. There is a relationship as follows:

$$T_2 = T_3, h_2 = h_3 \qquad \text{* MERGEFORMAT (S10)}$$

$$T_1 = T_4, h_1 = h_4 \qquad \text{* MERGEFORMAT (S11)}$$

In this case, the energy used to compress the working fluid in the thermal compression unit (Q_{re}) is exactly the total input energy consumption (Q_{in}).

Whether there is a high-temperature heat source or not, the thermodynamic efficiency (η) of the TC-CBC can be determined as follows:

$$\eta = P\tau / \left(Q_{in} \times M_{adsorbent}\right) \qquad \text{* MERGEFORMAT (S12)}$$

In this work, the adsorption of CO_2 is achieved at the ambient temperature of T_L, thus the thermodynamic perfection of the system is:

$$\varepsilon = \frac{P\tau}{\left(Q_{re} \times M_{adsorbent}\right)\left(1 - T_L/T_{H1}\right) + \left(Q_{heat} \times M_{adsorbent}\right)\left(1 - T_L/T_{H2}\right)} \text{*}$$

MERGEFORMAT (S13)

For the TC-CBC without a high-temperature heat source, the Q_{heat} in the denominator of Eq. (13) is equal to zero.

Under the temperature-pressure condition set in this work, the heat capacity of the CO_2 stream on the high-pressure side of the regenerator is higher than that on the low-pressure side regenerator. As a result, if the complete recovery is assumed, the temperature of exhaust gas will decrease to the temperature of T_2. The T_2' can be deduced by the conversation law of energy further:

$$h_{2'}\left(T_{2'}, p_H\right) - h_2 = h_4 - h_{4'}\left(T_2, p_L\right) \text{\textbackslash*MERGEFORMAT(S14)}$$

The Q_{heat} here is:

$$Q_{\text{heat}} = M_{CO_2} \times \left(h_3 - h_2 - \left(h_4 - h_{4'}\left(T_2, p_L\right)\right)\right) \Big/ M_{\text{adsorbent}} \text{ \textbackslash*}$$

MERGEFORMAT (S15)

Accordingly, the η and the ε are:

$$\eta = P\tau \Big/ \left(\left(Q_{re} + Q_{\text{heat}}\right) \times M_{\text{adsorbent}}\right) \text{\textbackslash* MERGEFORMAT (S16)}$$

$$\varepsilon = \frac{P\tau}{\left(Q_{re} \times M_{\text{adsorbent}}\right)\left(1 - T_L/T_{H1}\right) + \left(Q_{\text{heat}} \times M_{\text{adsorbent}}\right)\left(1 - T_L/T_{H2}\right)} \text{\textbackslash*}$$

MERGEFORMAT (S17)

S2. Evaluation of the TC-CBC

In this work, the lowest cycle temperature (T_L) and the lowest cycle pressure (p_L) were set as 308 K and 10 bar, respectively, which means that the adsorption occurs under a temperature of 308 K and a pressure of 10 bar. The desorption temperature (T_{H1}) of 393 K was used to represent low-grade heat sources. The equivalent isentropic compression process is assumed in the thermal compression unit:

$$s\left(T_L, p_L\right) = s\left(T_{H1}, p_H\right) \quad \text{\textbackslash* MERGEFORMAT (S18)}$$

Thus, the highest cycle pressure (p_H) can be calculated as 30.0088bar. If a high-temperature heat source is included, the temperature (T_{H2}) of 573 K was chosen to denote the high-grade heat sources. For the expander where the ideal adiabatic expansion process occurs, there is:

$$s\left(T_4, p_L\right) = s\left(T_{H_2}, p_H\right) \quad \text{\textbackslash* MERGEFORMAT (S19)}$$

Accordingly, the temperature (T_4) of working fluid at the expander outlet is 465.7K. All the thermodynamic parameters of working fluid in the power cycle loop can be

obtained in REFPROP [2] and the data are listed in the Table S1.

Table S1. Thermodynamic properties of working fluid in the power cycle loop.

Point	T (K)	p (MPa)	H (kJ·kg^{-1})	s (kJ·kg^{-1}·K^{-1})
1	308.0	10	506.21	2.3136
2	393.0	30.0088	575.06	2.3136
3	573.0	30.0088	764.15	2.7090
4	465.7	10	657.50	2.7090
2'	462.39	30.0088	646.58	2.4812
4'	393	10	585.98	2.5421

S3. Performance of the MOF-based TC-CBC from GCMC simulations

How the adsorption loading changes with the number of cycles for 3 representative MOFs is shown in Figure S4. It is clear that the total 10000 cycles are sufficient to obtain reliable results.
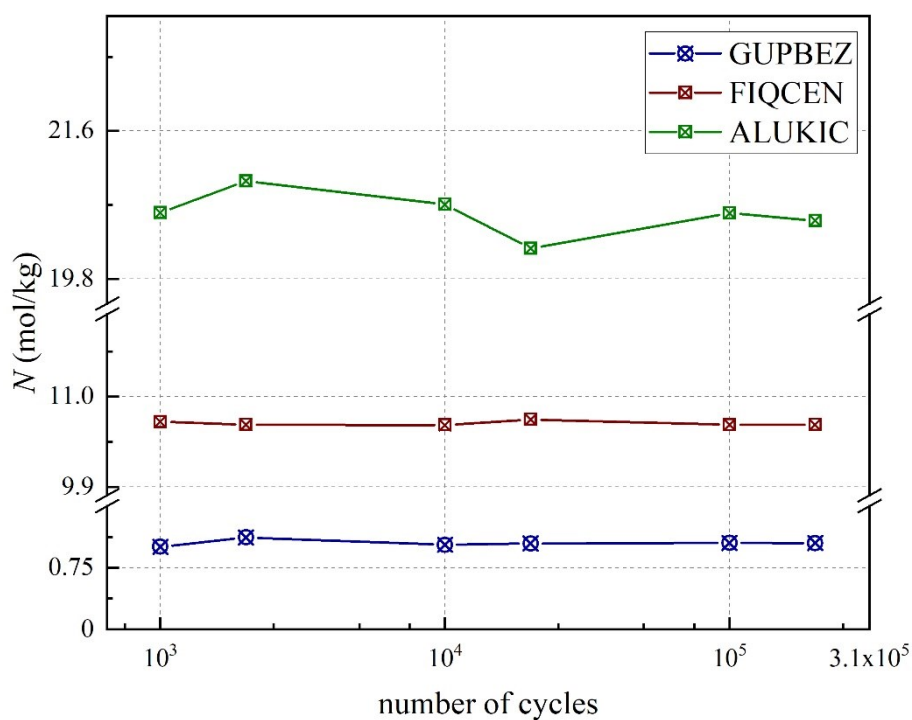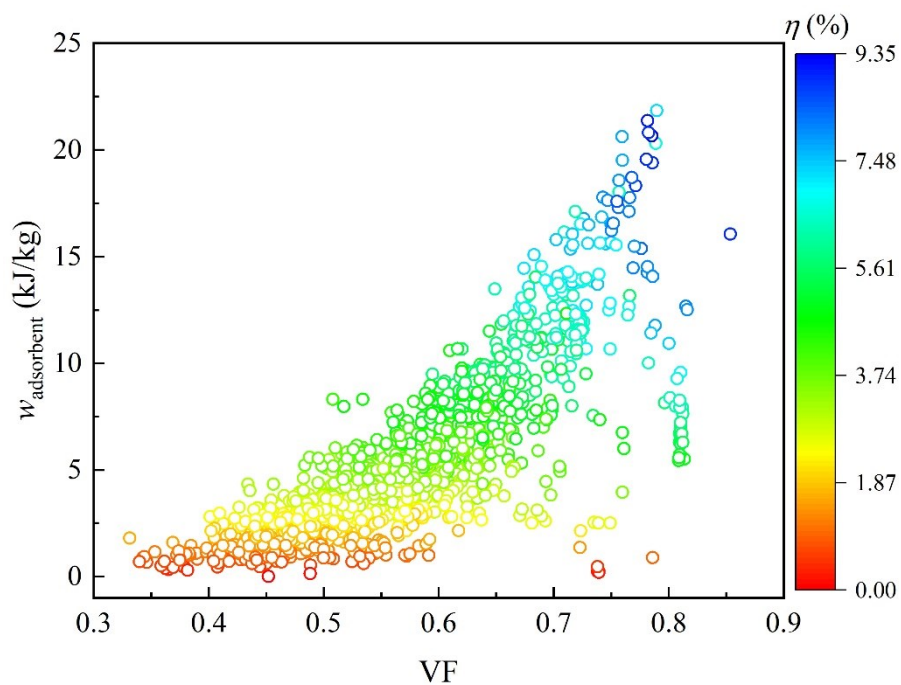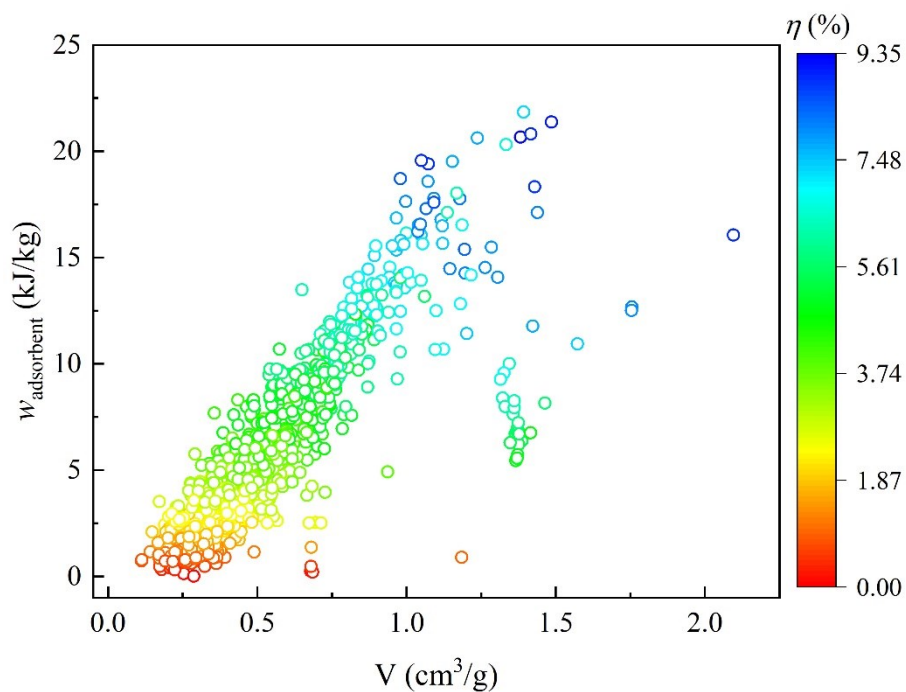
Figure S4. The adsorption loadings in 3 representative CoRE-MOFs using

different GCMC cycles.

(a)

(b)

Figure S5. The correlation between thermodynamic performances (η, $w_{\text{adsorbent}}$) and

structural properties: (b) VF; (c) V.

S4. Prediction of the thermodynamic performance of the MOF-based TC-CBC using ML model

Table S2. Chemical descriptors used in this work.

variable	note
C	number of carbon atoms per unit volume
H	number of hydrogen atoms per unit volume
O	number of oxygen atoms per unit volume
N	number of nitrogen atoms per unit volume
F	number of fluorine atoms per unit volume
Cl	number of chlorine atoms per unit volume
Br	number of bromine atoms per unit volume
Metal	number of metal atoms per unit volume
OMS	whether has open metal site (OMS) or not

References

[1] B.B. Saha, I.I. El-Sharkawy, K. Habib, S. Koyama, K. Srinivasan, Journal of Chemical & Engineering Data. 53 (2008) 1872-1876.

[2] L. EW, H. ML, M. MO.