Supplementary information

Near-Cryogenic Direct Air Capture using Adsorbents

Seo-Yul Kim,¹Akriti Sarswat,¹ Sunghyun Cho,² MinGyu Song,¹ Jinsu Kim,³ Matthew J. Realff,¹ David S. Sholl,⁴ and Ryan P. Lively^{1,*}

¹School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

²School of Chemical Engineering, School of Semiconductor and Chemical Engineering, Clean Energy Research Center, Jeonbuk National University, JeonJu, Jeonbuk 54896, Republic of Korea

³Department of Petrochemical Materials, Chonnam National University, 50 Daehak-ro, Yeosu-si, 59631, Republic of Korea

⁴Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

*Correspondence: ryan.lively@chbe.gatech.edu

Contents	Description
Supplemental item	S
Figure S1	Water saturation loading in air (RH = 100%) and a schematic illustration of the thermal coupling between LNG regasification and direct air capture (DAC)
Figure S2	Distribution of CO ₂ heat of adsorption in CoRE-MOF DDEC structures and their probability of having a Henry's constant > 0.1388 mol/kg/Pa
Figure S3	Violin plots of physical properties for adsorbents with suitable heats of adsorption for DAC at 160 K, 220 K, and 298 K
Figure S4	Violin plots of pore volume and largest cavity diameter for the 100 structures with the highest CO ₂ uptake at 40 Pa under 298 K, 220 K, and 160 K
Figure S5	Effect of heat of adsorption at 298 K and largest cavity diameter on the predicted saturation CO_2 loading of CoRE-MOF DDEC structures
Figure S6	Predicted saturation uptake and pore saturation degree of CoRE-MOF DDEC structures at 298 K and 220 K.
Figure S7	Distribution of physical properties for CoRE-MOF DDEC structures identified as promising DAC candidates at 160 K
Figure S8	Henry's constant for CO ₂ adsorption in MIL-120(Ga) and MIL-120(Al) at various temperatures predicted using MC simulations
Table S1	The first and third quartiles of physical properties for optimal structures for DAC at 298 K, 220 K, and 160 K
Table S2	Summary of guidelines for identifying promising near-cryogenic DAC sorbents based on molecular simulations of CoRE-MOF DDEC structures
Table S3	Near-cryogenic DAC performance of MIL-120(Ga) based on molecular simulations
Figure S9	PXRD patterns of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20
Figure S10	Nitrogen adsorption isotherms of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20 at 77 K
Table S4	BET surface area and pore volume of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20
Figure S11	Experimental CO ₂ adsorption isotherms of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20 under near-cryogenic conditions
Figure S12	Experimental CO ₂ and N ₂ adsorption isotherms of MIL-120(Al) at 160 K, Zeolite 5A at 220 K, and CALF-20 at 195 K
Figure S13	N_2 adsorption isotherms of Zeolite 13X at 180 K, 200 K, and 220 K. The data was curve-fitted using the dual-site Langmuir Freundlich equation
Figure S14	CO ₂ and N ₂ adsorption isotherms of Zeolite 13X at various temperature, and CO ₂ /N ₂ selectivity predicted by IAST
Figure S15	Schematic illustration of the experimental setup for fixed-bed adsorption/desorption using Zeolite 13X and CALF-20
Figure S16	CO ₂ adsorption isotherm of Zeolite 13X and CALF-20 at 195 K measured under a volumetric apparatus with high-vacuum activation
Figure S17	Breakthrough curve of Zeolite 13X bed and the bed temperature profile during the analysis
Figure S18	Breakthrough curve of CALF-20 bed and the bed temperature profile during the analysis
Figure S19	Outlet gas concentration profile and CO ₂ adsorption kinetics during breakthrough analysis of Zeolite 13X using a 1% CO ₂ mixture in an N ₂ balance
Figure S20	Pseudo-equilibrium capacity comparison during series of breakthrough analysis for Zeolite 13X and CALF-20 at 195 K
Figure S21	Normalized CO ₂ adsorptin kinetics of Zeolite 13X and CALF-20 fixed bed at 195 K
Figure S22	Ten sequential adsorption cycles for Zeolite 13X and CALF-20

Contents	Description			
Table S5	Shared parameters for DAC systems coupled with LNG regasification			
Table S6	Parameters for the LNG regasification process coupled with DAC systems			
Table S7	Parameters for the techno-economic analysis of amine sorbent-based ambient DAC system			
Table S8	Parameters for the techno-economic analysis of Zeolite 13X-based near-cryogenic DAC			
Table S9	Parameters for the techno-economic analysis of CALF-20-based near-cryogenic DAC			
Table S10	Other parameters for techno-economic analysis			
Figure S23	Effect of atmospheric air temperature on cold energy consumption for operating a near- cryogenic DAC process			
Figure S24	Impact of sorbent annual degradation rate on overall amine sorbent costs			
Figure S25	Required heat transfer area for operating the LNG-DAC process			
Figure S26	Estimated additional heat exchanger cost for LNG-DAC process			
Figure S27	Effect of $T_{NG,1}$ in Zeolite 13X-based LNG-DAC process on annualized CAPEX for heat exchanger and LNG consumption			
Figure S28	Process optimization strategies to minimize cold energy consumption in the LNG- DAC process and their estimated impacts			
Figure S29	Case comparison of Zeolite 13X-based near-cryogenic DAC and amine sorbent-based ambient DAC processes			
Table S11	Parameters for case comparison between ambient and near-cryogenic DAC			
Figure S30	Effect of capture efficiency on global LNG-DAC potential			
Figure S31	Effect of adsorption temperature on global LNG-DAC potential			
Figure S32	Global LNG-DAC potential projections			
Figure S33	Compressor work required for CO ₂ desublimation and near-cryogenic DAC			
Supplemental e	experimental procedures			
S1.	Supplemental simulation and experimental procedure			
S1.1.	Large-scale molecular simulation procedure			
S1.2.	Experimental procedure			
S2.	Candidate material selection for near-cryogenic DAC			
S3.	Techno-economic analysis of near-cryogenic DAC			
S3.1.	Energy duty calculations			
S3.2.	OPEX estimation			
S3.3.	CAPEX estimation			
S3.4.	Sorbent cost estimation			
S3.5.	Additional heat exchanger area estimation (LNG-DAC)			
S3.6.	Global LNG-DAC potential estimation			
\$3.7.	Energy estimation for external cooling cycle-based system			
References				

Supplemental items



Figure S1. (a) Water saturation loading in air at 100% relative humidity (RH) across a temperature range of 110 K to 303 K.¹ (b) Schematic illustration of the thermal coupling process between LNG regasification and near-cryogenic direct air capture (DAC).



Figure S2. (a) Distribution of CO₂ heat of adsorption for structures in the CoRE-MOF DDEC dataset. (b) Probability of structures having a Henry's constant greater than 0.1388 mol/kg/Pa at 298 K, 220 K, and 160 K.



Figure S3. Violin plots of adsorbents with suitable heat of adsorptions for DAC at 160 K, 220 K, and 298 K. The suitable heat of adsorption ranges were set as $37 < \Delta \hat{H}_s < -24$ (160 K), $-56 < \Delta \hat{H}_s < -40$ (220 K), and $-80 < \Delta \hat{H}_s < -60$ (298 K), respectively. (a) gravimetric surface area, (b) volumetric surface area, (c) pore limiting diameter, and (d) helium void fraction.



Figure S4. Violin plots showing (a) pore volume and (b) largest cavity diameter for the top 100 structures ranked by CO_2 uptake at 40 Pa, under various temperature conditions (298 K, 220 K, and 160 K). The yellow box highlights the range of properties that represent a potential new opportunity for adsorbents under near-cryogenic DAC conditions.



Figure S5. Effect of (a) heat of adsorption at 298 K and (b) largest cavity diameter on predicted saturation CO_2 loading of structures in CoRE-MOF DDEC database. The saturation loading was calculated by assuming that CO_2 fully occupies the total pore volume of the structures, and that CO_2 has the same density as liquid CO_2 at 298 K.



Figure S6. Predicted saturation uptake (q_{sat} , green line) and degree of pore saturation (q/q_{sat} , red line) of structures in CoRE-MOF DDEC database at 298 K and 220 K. The saturation loading was calculated by assuming that CO₂ fully occupies the total pore volume of the structures, and that CO₂ has the same density as liquid CO₂ at given temperatures. The plot was drawn using the Locally Weighted Scatterplot Smoothing (Lowess) method for scattered data for CoRE-MOF DDEC.



Figure S7. Distribution of physical properties for CoRE-MOF DDEC structures identified as promising candidates for DAC at 160 K. (a) Crystal density vs. total volumetric surface area, (b) total gravimetric surface area vs. largest cavity diameter, (c) pore limiting diameter vs. total pore volume, and (d) crystal density vs. helium void fraction. Green symbols highlight the properties of four selected near-cryogenic DAC sorbents: MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20. The curves along the top and right edges of each graph represent distribution profiles generated using kernel smoothing. Dashed-line-highlighted areas denote the range of physical properties found to be optimal for near-cryogenic DAC conditions in Table S2.



Figure S8. Henry's constant for CO₂ adsorption in MIL-120(Ga) (UVEXAV in CoRE-MOF DDEC) and MIL-120(Al) (BUSQIQ in CoRE-MOF2019) at various temperatures predicted using GCMC simulation. The simulation for MIL-120(Al) was conducted after assigning atomic charges using DDEC method.

Condition the optimal structures were selected under	Cry den (g·c	vstal usity em ⁻³)	Pore v (cc)	olume g ⁻¹)	Largest diam (Å	cavity neter A)	Pore lin diam (Å	miting neter A)	Gravir surfac (m ² ·	netric e area g ⁻¹)	Volun surfac (m ² ·c	netric e area cm ⁻³)	Helium vo	id fraction
	l st quartile	3 rd quartile	1 st quartile	3 rd quartile	1 st quartile	3 rd quartile	1 st quartile	3 rd quartile	1 st quartile	3 rd quartile	1 st quartile	3 rd quartile	1 st quartile	3 rd quartile
298 K	1.50	1.92	0.249	0.346	4.73	5.62	3.71	4.24	439	910	774	1460	0.467	0.569
220 K	1.13	1.60	0.302	0.523	4.87	6.52	3.64	4.86	478	1570	799	1880	0.472	0.617
160 K	1.04	1.47	0.329	0.560	5.02	7.16	3.86	5.48	549	1580	822	1700	0.469	0.610
All structures in CoRE-MOF DDEC	1.03	1.51	0.327	0.592	5.04	7.31	3.86	5.72	574	1680	858	1790	0.481	0.624
Average (220 K and 160 K)	1.08	1.54	0.315	0.542	4.94	6.84	3.75	5.17	514	1570	810	1790	0.471	0.613

Table S1. The first and third quartiles of physical properties for optimal structures for DAC at 298 K, 220 K, and 160 K in comparison with those for all structures in CoRE-MOF DDEC.

Candidates	Cry den (g·c	rstal sity m ⁻³)	Po	ore volum (cc·g ⁻¹)	ie	La	rgest ca diamete (Å)	vity r	Pore dia	limiting umeter (Å)	Gravi surfac (m ²	metric ce area ·g ⁻¹)	Volu surfac (m ² ·	metric ce area cm ⁻³)	Heliur frac	n void tion
	1 st quartile	3 rd quartile	1^{st}	3 rd	Extra*	1 st	3 rd	Extra*	1^{st}	3 rd	1^{st}	3 rd	1^{st}	3 rd	1^{st}	3 rd
	1.08	1.54	0.315	0.542	0.73 ~1.55	4.94	6.84	9.7 ~16.1	3.75	5.17	514	1570	810	1790	0.471	0.613
MIL-120(Al)	1.	57		0.275			4.49			3.69	6	14	9	63	0.4	-32
Zeolite 5A	1.4	2**		0.298			9.53		÷	3.86	6	77	9	62	0.4	24
Zeolite 13X	1.	41		0.322			10.4		4	5.89	8	71	12	230	0.5	03
CALF-20	1.	38		0.403			5.06		4	4.39	5	83	8	03	0.5	60

Table S2. Summary of guidelines for identifying promising near-cryogenic DAC sorbents based on molecular simulations of CoRE-MOF DDEC structures.

*Physical property region suggested for high CO₂ uptake/working capacity under near-cryogenic DAC condition. **Physical property that satisfies the criteria appears in italics and bold text.

Table S3. Near-cryogenic DAC performance of MIL-120(Ga) based on molecular simulations.

	$\frac{\Delta \widehat{H}_s}{(\text{kJ/mol})}$	K _{H_CO2,160 K} (mol/kg/Pa)	K _{H_N2,160 K} (mol/kg/Pa)	K _{H_CO2} /K _{H_N2} , at 160 K	K _{H_CO2,220 K} (mol/kg/Pa)	q _{C02,220 К} (mmol/g)
MIL-120(Ga)	-52.0	$2.99 \cdot 10^{6}$	0.167	$1.79 \cdot 10^{7}$	62.7	3.53



Figure S9. PXRD patterns of (a) synthesized MIL-120(Al) and prepared Zeolites, and (b) CALF-20.



Figure S10. Nitrogen adsorption isotherms of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20 at 77 K.

	BET surface area (m^2/g)	Total pore volume (cm ³ /g)*
MIL-120(Al)	297	0.294
Zeolite 5A	719	0.287
Zeolite 13X	695	0.275
CALF-20	509	0.196

 Table S4. BET surface area and pore volume of MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20.

*Calculated from single point adsorption at around $P/P_0=0.95$



Figure S11. Experimental CO₂ adsorption isotherms of (a) MIL-120(Al), (b) Zeolite 5A, (c) Zeolite 13X, and (d) CALF-20 under near-cryogenic conditions (160 K–220 K), measured using a volumetric apparatus and a cryogenic temperature controller.



Figure S12. Experimental CO_2 and N_2 adsorption isotherms of (a) MIL-120(Al) at 160 K, (b) Zeolite 5A at 220 K, and (c) CALF-20 at 195 K, along with fitted curves using the dual-site Langmuir Freundlich equation for calculating IAST selectivity.



Figure S13. Experimental N_2 adsorption isotherms of Zeolite 13X at 180 K, 200 K, and 220 K. The data was curve-fitted using the dual-site Langmuir Freundlich equation.



Figure S14. Experimental CO₂ and N₂ adsorption isotherms of Zeolite 13X (a) at 180 K, (c) at 200 K, and (e) at 220 K and fitted curve using dual-site Langmuir Freundlich equation. Adsorption behavior of CO₂ and N₂ from CO₂/N₂ mixture (4/9996) predicted by IAST (b) at 180 K, (d) at 200 K, and (f) at 220 K.



Figure S15. (a) Schematic illustration of the breakthrough analysis for Zeolite 13X and CALF-20 under near-cryogenic DAC conditions (195 K). (b) Experimental setup for Zeolite 13X desorption using inert gas (He) flow at 473 K. (c) Experimental setup for CALF-20 desorption under vacuum (~0.08 bar) at approximately 293 K.



Figure S16. CO₂ adsorption isotherm of Zeolite 13X and CALF-20 at 195 K measured under a volumetric apparatus with high-vacuum activation. The adsorption cell temperature was maintained during the measurement using a dry ice/acetone cooling bath.



Figure S17. Breakthrough curves and bed surface temperatures for Zeolite 13X under (a) 100 sccm of 400 ppm CO_2 in He balance, (b) 200 sccm of 400 ppm CO_2 in He balance, (c) 100 sccm of 400 ppm CO_2 in N₂ balance, and (d) 200 sccm of 400 ppm CO_2 in N₂ balance.



Figure S18. Breakthrough curves and bed surface temperatures for CALF-20 under (a) 100 sccm of 400 ppm CO_2 in N_2 balance, and (b) 200 sccm of 400 ppm CO_2 in N_2 balance.



Figure S19. (a) Gas concentration profile from breakthrough analysis of Zeolite 13X under nearcryogenic DAC conditions (195 K) using a 1% CO_2 mixture in an N₂ balance at 50 sccm. (b) CO_2 adsorption kinetics during breakthrough analysis of Zeolite 13X with a 1% CO_2 mixture in an N₂ balance.



Figure S20. Pseudo-equilibrium capacity comparison during series of breakthrough analysis for Zeolite 13X and CALF-20 at 195 K.



Figure S21. Normalized CO₂ uptakes of Zeolite 13X and CALF-20 fixed bed during breakthrough analysis at 195 K under 100 sccm of simulated dry air (400 ppm CO₂/balance N₂).



Figure S22. Ten sequential adsorption cycles for Zeolite 13X (a-c) and CALF-20 (e-f). (a) 1st, 2nd, and 3rd adsorption breakthrough curves of Zeolite 13X at 195 K using 400 ppm CO₂/N₂ under various flow rates (400, 570, and 1000 sccm). (b) 3rd to 10th adsorption breakthrough curves of Zeolite 13X at 195 K using 1000 sccm of 400 ppm CO₂/N₂. (c) Comparison of pseudo-equilibrium adsorption capacity ($q_{pseudo-eq}$, calculated at C/C₀=0.95) of Zeolite 13X during ten cyclic adsorption runs. (d) 1st, 2nd, and 3rd adsorption breakthrough curves of CALF-20 at 195 K using 400 ppm CO₂/N₂ under various flow rates (400, 570, and 800 sccm). (e) 3rd to 10th adsorption breakthrough curves of CALF-20 at 195 K using 800 sccm of 400 ppm CO₂/N₂. (f) Comparison of pseudo-equilibrium adsorption capacity of CALF-20 during ten cyclic adsorption runs. Desorption was conducted under N₂ flow for 20 minutes at 200 °C for Zeolite 13X and 90 °C for CALF-20, respectively.

Parameter	Description	Value	Reference
T _{ads}	Adsorption temperature of LNG-DAC	195 K	
T_{h1}	System temperature achieved by heat exchange with seawater	283 K	
M _{air}	Average molecular weight of dry air	28.96 g/mol	
C_{p,CO_2}	Specific heat of CO ₂ in constant pressure	0.851 kJ/kg·K	2
$C_{p,air}$	Specific heat of dry air	1.004 kJ/kg·K	2
$C_{p,water}$	Specific heat of water vapor	1.996 kJ/kg·K	2
$\Delta \widehat{H}_{water,con}$	Heat of water condensation	2256 kJ/kg	2
U _{air-air}	Overall heat transfer coefficient of air-air heat exchanger	35 W/m²/K	3-5
V_{CO_2}	Price of high-purity CO ₂	51 USD/tonnes	6
$\eta_{ ext{cap}}$	Carbon capture efficiency of process	60% or calculated from mass-transfer coefficient	
CI _{thrm}	Carbon intensity of thermal energy	5-56 kgCO ₂ /GJ	7
Cl _{elec}	Carbon intensity of electrical energy	12 kgCO ₂ /MWh	
P _{atm}	1013.25	mbar	

 Table S5. Shared parameters for DAC systems coupled with LNG regasification.

Parameter	Description	Value	Reference
$T_{NG,1}$	NG temperature after heat exchange with DAC system	~283 K	
$\Delta \widehat{H}_{NG,evap}$	Enthalpy change of NG (methane) during evaporation	511.35 kJ/kg NG	2
$\Delta \widehat{H}_{heating,1}$	Enthalpy change of NG (methane) during heating from 109.1 K to $T_{NG,1}$.	H _{TNG,1} ,1 bar - H _{109.1} K,1 bar	2
$\Delta \widehat{H}_{heating,2}$	Enthalpy change of NG (methane) during heating from $T_{NG,1}$ to 283 K.	H _{283 K,1 bar} - H _{TNG,1} ,1 _{bar}	2
$U_{evap,air}$	Overall heat transfer coefficient of air heat exchanger for evaporation of LNG	44.5-95.8 W/m ² /K	8,9
$U_{heating,air}$	Overall heat transfer coefficient of air heat exchanger for heating NG to $T_{NG,1}$	100-130 W/m²/K	8, 9
$U_{evap,water}$	Overall heat transfer coefficient of seawater heat exchanger for evaporation of LNG	630 W/m ² /K	10, 11
$U_{heating,water}$	Overall heat transfer coefficient of seawater heat exchanger for heating NG to 283 K	850 W/m ² /K	10-12
\dot{m}_{LNG}	Mass flow rate of LNG (1 kg Zeolite 13X, 1cycle/h)	kg/h	
\dot{m}_{CO_2}	Mass flow rate of produced CO ₂ (1 kg Zeolite 13X, 1cycle/h)	kg/h	
M_{LNG}	Global regasification capacity	$Mt_{LNG}/year$	
M_{CO2}	Global LNG-DAC potential	Mt _{CO2} /year	

Table S6. Parameters for the LNG regasification process coupled with DAC systems.

Parameter	Description	Value	Reference	
T _{ads}	Adsorption temperature	298 K	13	_
T _{des}	Desorption temperature	383 K	13	
WC	Working capacity of an amine sorbent under DAC TVSA	$0.0748 \ g_{CO2}/g_{ads}/cycle$	14	
$C_{p,amine}$	Specific heat of an amine sorbent	1.7 kJ/kg·K	15	
$\Delta \widehat{H}_{s,amine,CO_2}$	Heat of adsorption for CO ₂ for an amine sorbent	2045 J/g _{CO2}	16	
$\Delta \widehat{H}_{s,amine,H_20}$	Heat of adsorption for water for an amine sorbent	2970 J/g _{H20}	17	
C _{ads}	Sorbent price of an amine sorbent	2.7 USD/kg	18	
r_{H_2O/CO_2}	Ratio of water working capacity over CO ₂ working capacity	6.3 kg _{H20} /kg _{C02}	17	
r_{deg}	Annual degradation rate	50%/year		
$\eta_{ m lat,rec}$	Water latent heat recovery efficiency	0.7		
P _{vac}	Target vacuum pressure during desorption	100 mbar		
r_{comp}	Compression ratio of moisture after the condensation	2	19	
k	Mass transfer coefficient	0.005 m/s		

Table S7. Parameters for the techno-economic analysis of amine sorbent-based ambient DAC system.

Parameter	Description	Value	Reference
T _{des}	Desorption temperature	473 K	
WC	Working capacity of Zeolite 13X in LNG-DAC	$0.22 \ g_{CO2}/g_{ads}$ /cycle	This work
$C_{p,13x}$	Specific heat of Zeolite 13X	0.943 kJ/kg·K	20
$\Delta \widehat{H}_{s,13X,CO_2}$	Heat of adsorption for CO ₂ in Zeolite 13X	861.4 J/g	21
C _{ads}	Sorbent price of Zeolite 13X	0.85 USD/kg	
$r_{H_20/C0_2}$	Ratio of water working capacity over CO ₂ working capacity	$0 \ kg_{\rm H2O}/kg_{\rm CO2}$	
r_{deg}	Annual degradation rate	0%/year	
$\eta_{ m lat,rec}$	Water latent heat recovery efficiency	0	
k	Mass transfer coefficient	0.004 m/s	

 Table S8. Parameters for the techno-economic analysis of Zeolite 13X-based near-cryogenic DAC.

Table S9. Parameters for the techno-economic analysis of CALF-20-based near-cryogenic DAC.

Parameter	Description	Value	Reference
T _{des}	Desorption temperature	283 K	
WC	Working capacity of CALF-20 in LNG-DAC	$0.082 \ g_{CO2}/g_{ads}/cycle$	This work
C _{ads}	Sorbent price of CALF-20	20 USD/kg	22
r_{H_2O/CO_2}	Ratio of water working capacity over CO ₂ working capacity	$0 \ kg_{H2O}/kg_{CO2}$	
r_{deg}	Annual degradation rate	0%/year	
$\eta_{ m lat,rec}$	Water latent heat recovery efficiency	0	
P _{vac}	Target vacuum pressure during desorption	100 mbar	
k	Mass transfer coefficient	0.004 m/s	

Parameter	Description	Value or unit	Reference
η_{fan}	Fan efficiency	0.614	19
η_{vac}	Vacuum efficiency	0.5	19
η_{thrm}	Thermal energy efficiency	0.85	23
η_{grid}	Electrical energy efficiency	0.4	23
Q _{loss}	Heat loss during sensible and latent heat supply	0.1	19
C_{elec}	Unit cost of electrical energy (grid)	30 USD/MWh	19
C_{thrm}	Unit cost of thermal energy (NG)	3.5 USD/GJ*	24
k	Overall mass transfer coefficient	0.005 m/s (at 298 K)	25
C_{equip}	Total equipment cost	USD	
C_{cont}	Contactor cost	USD/kg _{ads}	
A_{cont}	Contactor cross-sectional area	m^2	
A _{hex,total}	Total heat exchanger surface area	m^2	
C_{CO_2}	CO ₂ concentration in atmospheric air	$0.719 g_{CO2} / m^3{}_{air}$	
C _{ads}	Sorbent price	USD/kg _{ads}	
$C_{hex,area}$	Unit cost per area of heat exchanger	100 USD/m ²	26
C_{hex}	Equipment cost of heat exchanger	USD	
$C_{fan,ref}$	Equipment reference cost for fan	2000 USD	19
C_{fan}	Equipment cost of fan	USD	19
C_{vac}	Equipment cost of vacuum pump	USD	27
\dot{F}_{vac}	Inlet flow rate of vacuum pump	m³/h	27
a _{coef}	vacuum pump cost estimation coefficient	423.9	19, 27
b _{coef}	vacuum pump cost estimation coefficient	0.653	19, 27
C _{coef}	vacuum pump cost estimation coefficient	30000	19, 27
E_{fan}	Electrical energy duty from fan	GJ/year	
E_{vac,CO_2}	Electrical energy duty from vacuuming CO ₂	GJ/year	
E_{vac,H_2O}	Electrical energy duty from vacuuming H ₂ O	GJ/year	

 Table S10. Other parameters for techno-economic analysis.

F_{air}	Air flow rate	m^3_{air}/s	
F _{air,ref}	Air flow rate at reference scale	$1.77 \ m^3_{air}/s$	19
f _{ann}	Multiplication factor of the annualization	-	
IR	Interest rate	0.08	27
y_f	Operation period of the DAC plant	15 year	23
$M_{DACscale}$	Annual CO ₂ capture scale	8760 tCO ₂ /year	
N_{cycle}	Number of cycles per year	8760 cycle/year	
r_{A2V}	Surface area to volume ratio	$469.6 \text{ m}^2/\text{m}^3$	19
ΔP	Pressure drop	100 Pa	19
v_{air}	Air velocity	2 m/s	
h	Contactor height	1 m	18
R	Ideal gas constant	8.314 J/mol/K	
Q_{sen,H_2O}	Sensible heat for water	GJ/year	
Q_{sen,CO_2}	Sensible heat for CO ₂	GJ/year	
Q_{lat,H_2O}	Latent heat for water	GJ/year	
Q_{lat,CO_2}	Latent heat for CO ₂	GJ/year	
$Q_{sen,ads}$	Sensible heat for adsorbent	GJ/year	
Q_{sum}	Sum of thermal energy duty	GJ/year	
Q_{total}	Total thermal energy duty (considering energy efficiency)	GJ/year	
E _{sum}	Sum of electrical energy duty	GJ/year	
E _{total}	Total electrical energy duty (considering energy efficiency)	GJ/year	
OPEX	Annual operating expenditure	USD/year	
<i>OPEX_{ads}</i>	Sorbent replacement cost	USD/year	
CAPEX	Total capital expenditure	USD	
CAPEX _{equip}	Total capital expenditure for equipment	USD	
CAPEX _{bed}	Total capital expenditure for sorbent bed	USD	
$CAPEX_{ads}$	Capital expenditure for sorbent	USD	
CAPEX _{cont}	Capital expenditure for contactor	USD	
CAPEX _{ann}	Annualized capital expenditure	USD/year	
CAPEX _{fan,ann}	Annualized capital expenditure for fan	USD/year	

CAPEX _{vac,ann}	Annualized capital expenditure for vacuum pump	USD/year	
CAPEX _{hex,ann}	Annualized capital expenditure for heat exchanger	USD/year	
CAPEX _{bed,ann}	Annualized capital expenditure for sorbent bed	USD/year	
E_{cold}	Total cold energy duty	GJ/tCO ₂	
E _{air,c}	Cold energy duty from dry air cooling	GJ/tCO ₂	
E _{humid,c}	Cold energy duty from humidity condensation	GJ/tCO ₂	
E _{ads,c}	Cold energy duty from adsorbent cooling	GJ/tCO ₂	
E _{hoa,c}	Cold energy duty from removing heat generated from adsorption	GJ/tCO ₂	
M _{ads}	Sorbent mass	kg	
f_{deg}	Correction factor for the sorbent degradation	-	
wc _{act}	Actual CO ₂ working capacity	$gCO_2/g_{ads}/cycle$	
WC _{act,aver}	Average CO ₂ working capacity until replacement	$gCO_2/g_{ads}/cycle$	
WC _{act,opt}	Average CO ₂ working capacity until optimal replacement time	$gCO_2/g_{ads}/cycle$	
WC	CO ₂ working capacity without degradation	$gCO_2/g_{ads}/cycle$	
\mathcal{Y}_{MU}	Sorbent replacement period	year	
$\mathcal{Y}_{MU,opt}$	Optimal sorbent replacement period	year	
f _{ads}	Correction factor for sorbent fabrication	3	18
f_{cont}	Correction factor for contactor fabrication	3	18
f _{тсі}	Multiplication factor of the total equipment capital investment	3.06	28
D_k	Knudsen diffusivity	m^2/s	
δ	Diffusion path length	m	
$\eta_{c,rec}$	Cold air enthalpy recovery efficiency	0.9	29, 30
LCOC	Levelized cost of capture	USD/tCO ₂	
EI	Energy intensity	GJ/tCO ₂	

*Four-year averaged Henry Hub natural gas spot price (1.4.2021~12.31.2024)



Figure S23. Effect of atmospheric air temperature on cold energy consumption for operating a nearcryogenic DAC process at 195 K. The capture efficiency (η_{cap}) was assumed to be 0.6, and no cold energy recovery was considered ($\eta_{c,rec}=0$).



Figure S24. Impact of the annual degradation rate of amine sorbents on total LCOC. (a) Effect of sorbent replacement time on LCOC for sorbent inventory and replacement under different annual degradation rate assumptions. (b) LCOC for sorbent inventory and replacement under various annual degradation rate assumptions, considering the optimal replacement time for each degradation condition.



Figure S25. Required heat exchanger area for operating the LNG-DAC process with 1 kg of Zeolite 13X, assuming a single cycle per hour (220 g CO₂/hr). The estimation was performed for various target temperatures of natural gas after heat exchange with the DAC system ($T_{NG,1}$). The required heat exchanger area for gasifying the same amount of LNG using an ambient air vaporizer (AAV) and an open rack vaporizer (ORV) is also shown for comparison. Capture efficiency (η_{cap}) was assumed to be 0.6, and cold energy recovery was not considered (η_{crec} =0).



Figure S26. Estimated additional heat exchanger cost for LNG-DAC coupling (195 K adsorption, η_{cap} =0.6, no cold energy recovery) to capture 1 tCO₂/hr using Zeolite 13X, compared to ORV. The market price of high-purity CO₂ was set at 51 USD/tCO₂.⁶



Figure S27. Effect of $T_{NG,1}$ in Zeolite 13X-based LNG-DAC process (1 tCO₂/hr, 195 K adsorption) on annualized CAPEX for heat exchanger and LNG consumption. The capture efficiency (η_{cap}) was assumed to be 0.6, and cold energy recovery was not considered ($\eta_{c,rec}$ =0).



Figure S28. Process optimization strategies to minimize cold energy consumption in the LNG-DAC process and their estimated impacts. (a) Integration of CO₂ emissions from NG combustion, used to generate thermal energy for LNG-DAC operation, into the DAC feed stream. (b) Cold energy recovery from downstream air to fresh feed air using an additional heat exchanger. (c) Combined effect of the two strategies on global LNG-DAC potential. Empty symbols indicate the case with the integration of emitted CO₂ from NG combustion. The adsorption temperature for the Zeolite 13X-based LNG-DAC process was set at 195 K (η_{cap} =0.6). Global LNG-DAC potentials were estimated based on the reference case in international LNG import outlooks from the U.S. Energy Information Administration.³¹ (d) Impact of cold energy recovery efficiency on the levelized capital cost of the additional heat exchanger in the Zeolite 13X-based LNG-DAC coupling process.



Figure S29. Case comparison of Zeolite 13X-based near-cryogenic DAC and amine sorbent-based ambient DAC processes. Scenarios were configured to simultaneously favor the ambient DAC process and disadvantage the near-cryogenic DAC process. The cost comparison is presented for two cases: (a) considering the five most influential parameters—mass transfer coefficient, heat exchanger unit cost, working capacity, and thermal and electrical energy costs—and (b) considering all 16 parameters used in the sensitivity analysis shown in Figure 5E. Refer to Table S11 for the specific values of each parameter.

	Reference case	Ambient (favorable case)	Near-cryogenic (unfavorable case)	Ambient (best case)	Near-cryogenic (worst case [*])
η_{fan}	0.614	0.614	0.614	0.614	0.614
η_{vac}	0.5	0.5	0.5	0.6	0.6
η_{thrm}	0.85	0.85	0.85	0.95	0.95
Q_{loss}	0.1	0.1	0.1	0.05	0.05
η_{grid}	0.4	0.4	0.4	0.48	0.48
C _{ads}	2.7/0.85	2.7	0.85	1.35	1.275
$C_{hex,area}$	100	-	120	-	120
C_{elec}	30	10	10	10	10
C_{thrm}	3.5	1	1	1	1
k	0.005/0.004	0.01	0.001	0.01	0.001
C_{cont}	25	25	25	12.5	12.5
$\Delta \widehat{H}_{s,H_20}$	53.5	53.5	-	40	-
r_{H_2O/CO_2}	6.3	6.3	-	5.04	-
wc	1.7/5.0	2.04	4.0	2.04	4.0
r_{deg}	50%	50%	-	30%	-
$\eta_{ m lat,rec}$	0.7	0.7	-	0.9	-

Table S11. Parameters for case comparison between ambient and near-cryogenic DAC.

*Economic parameters that commonly used for both systems were set following the best case scenario for ambient DAC **Values that differ from the reference value are highlighted in bold



Figure S30. Effect of capture efficiency (η_{cap}) of DAC side in Zeolite 13X-based LNG-DAC process on global LNG-DAC potential. The temperature of the adsorption process was set to 195 K. Both cold energy recovery ($\eta_{c,rec}$ =0.95) and integration of emitted CO₂ from NG combustion were considered. The global LNG-DAC potentials were estimated based on reference case of international LNG imports outlooks from the U.S. Energy Information Administration.³¹



Figure S31. Effect of adsorption temperature on global LNG-DAC potential. Capture efficiency was set as 0.6 (open symbols) and 0.9 (closed symbols). Both cold energy recovery ($\eta_{c,rec}$ =0.95) and integration of emitted CO₂ from NG combustion were considered. The global LNG-DAC potentials were estimated based on reference case of international LNG imports outlooks from the U.S. Energy Information Administration.³¹



Figure S32. (a) Global LNG-DAC potential estimated based on international LNG trade outlooks from the U.S. Energy Information Administration, IEO2023 (INTERNATIONAL ENERGY OUTLOOK 2023).³¹ The prediction considered probable advancement of LNG-DAC technology to reduce LNG consumption, namely, high adsorption temperature (240 K), high capture efficiency ($\eta_{c,rec}$ =0.9), integration of emitted CO₂ from NG combustion, and cold energy recovery ($\eta_{c,rec}$ =0.9). The line represents reference case projection. The shaded region represents the maximum and minimum values across the cases in IEO2023. (b-c) Global LNG-DAC potential prediction in (b) 2030 and (c) 2050 under various cold energy recovery efficiency. The probable contribution of cold energy from hydrogen and ammonia trade and use for shipping fuel is also reflected in 2050.³²



Figure S33. Compressor input work required for (a) CO_2 desublimation in the deposition chamber^{29, 30} and (b) operating near-cryogenic DAC at various atmospheric temperatures. The temperatures shown represent conditions prior to radiation cooling.

S1. Supplemental simulation and experiment procedure

S1.1. Large-scale molecular simulation procedure

The CoRE-MOF DDEC³³ is a subset of the 5,109 structures in CoRE-MOF 2014,³⁴ whose atomic charges were assigned using the DFT-based DDEC method³⁵ (**Figure 2A**). Large-scale molecular simulations were conducted exclusively on the CoRE-MOF DDEC structures, as accurate atomic charges are essential for the precise prediction of CO₂ adsorption.³⁶ The Zeo++ package³⁷ was used to determine the pore-limiting diameter (PLD), largest cavity diameter (LCD), gravimetric surface area (GSA), volumetric surface area (VSA), pore volume (V_p), and helium void fraction. Materials with a PLD smaller than 3.3 Å were excluded from further consideration due to potential diffusion limitations for CO₂. This approach identified 1,984 structures for Widom insertion simulations and grand canonical Monte Carlo (GCMC) simulations to evaluate the potential of physisorbents for near-cryogenic DAC.

Molecular simulations for CO₂ and N₂ adsorption were conducted using RASPA 2.0.³⁸ All simulations assumed rigid MOF structures. The Lennard–Jones (LJ) potential was used to model van der Waals interactions between atoms, with LJ parameters for framework atoms assigned according to the UFF force field.³⁹ The TraPPE model⁴⁰ was employed for adsorbate molecules, and force field parameters for adsorbate-framework interactions were defined using standard combining rules. A cutoff distance of 12.8 Å was applied, with interactions beyond this distance shifted to zero. Coulomb interactions were approximated using Ewald summation with a precision of 10⁻⁶. The combination of the UFF force field and TraPPE model has been widely used in molecular simulations for CO₂ capture.⁴¹⁻⁴⁷

For each structure, 2×10^5 cycles of Widom insertion were performed to calculate Henry's constant and heat of adsorption at 160, 220, and 298 K. For GCMC simulations, 10^5 initialization cycles were followed by 10^5 data collection cycles to determine CO₂ uptake at 220 and 298 K. GCMC simulations assigned equal probabilities to swap, translation, rotation, and reinsertion moves.

MIL-120(Ga) (structure code UVEXAV) ⁴⁸ was identified as a high-performing MOF under nearcryogenic DAC conditions. However, due to limited reports on its synthesis and stability, its betterknown isostructural MOF, MIL-120(Al), was considered a more practical synthetic candidate. To verify if MIL-120(Al) also exhibits comparable performance to MIL-120(Ga), the crystallographic structure of MIL-120(Al) was obtained from the CoRE-MOF 2019 database (structure code BUSQIQ),⁴⁹ as it was not included in the CoRE-MOF DDEC database.⁵⁰ For comparison with MIL-120(Ga) (UVEXAV) in the CoRE-MOF-DDEC database, atomic charges for BUSQIQ were assigned using the DDEC method. For both structures, Henry's constants for CO₂ adsorption were calculated using Widom insertion simulations over a temperature range of 130–300 K.

In contrast, Zeolite 5A, Zeolite 13X, and CALF-20 were selected based on their physical properties, which align with the structure-property guidelines derived from the simulation results (see Table S2 and Section S2 in the Supplemental Experimental Procedure). The physical properties of Zeolite 5A and Zeolite 13X were calculated using Zeo++, with structures generated through an interpolation method.⁵¹ Silica LTA frameworks were modified by interpolation to achieve an Si/Al ratio of 1, following Lowenstein's rule.⁵² Ca ions were added to maintain charge neutrality, with their positions determined using parallel tempering. The crystallographic structure of CALF-20 was obtained from its original report.⁵³

S1.2. Experimental procedure

S1.2.1. Materials

Zeolite 13X (powder, ~2 µm avg. particle size) and Zeolite 5A (powder, undried) were purchased from MilliporeSigma (US) and used without further treatment. Al(NO₃)₃·9H₂O (ACS reagent, \geq 98%), 1,2,4,5-benzenetetracarboxylic acid (for synthesis, \geq 98.0%), sodium hydroxide (ACS reagent, \geq 97.0%, pellets), Zn(OAc)₂·2H₂O (ACS reagent, \geq 98%), sodium oxalate (ACS reagent, \geq 99.5%), 1,2,4-triazole (for synthesis, \geq 98.0%), and methanol (\geq 99.8%, ACS reagent) were purchased from MilliporeSigma (US).

S1.2.2. Synthesis

MIL-120(Al) was synthesized following the reported procedure.⁴⁹ Briefly, 3.4 ml of NaOH solution (4M) and 10 ml of deionized water were poured into 3.2 g of Al(NO₃)₃·9H₂O to dissolve the metal precursor and make a homogeneous solution. 0.5 g of 1,2,4,5-benzenetetracarboxylic acid was dissolved in 10 ml of deionized water in another vial, and the two solutions were mixed in a 100 ml Teflon-lined hydrothermal autoclave. The reaction was conducted at 210 °C for 24 h. After the reaction, white powder (~0.5 g) was collected via centrifuge. The sample was washed by reflux with 500 ml of water for 12 h. At last, the sample was dried in an oven at 60 °C overnight.

CALF-20 was synthesized following the reported procedure.⁵⁴ Briefly, $Zn(OAc)_2 \cdot 2H_2O$ was dissolved in 20 mL of an aqueous methanol solution (4:1, v/v) and stirred for 5 minutes to obtain a clear solution. Sodium oxalate was then added, and the mixture was stirred for an additional 5 minutes, resulting in a suspension of Zn-oxalate particles. Subsequently, 1,2,4-triazole was introduced into the suspension, and the mixture was stirred for 50 minutes. The product was collected by centrifugation and thoroughly washed with distilled water six times. Finally, it was dried at 100 °C in air overnight.

S1.2.3. Sample characterization

Powder X-ray diffraction (PXRD) patterns ($4^{\circ} < 2\theta < 70^{\circ}$) of four prepared samples, MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20 were recorded using Rigaku Miniflex Powder XRD instrument (Rigaku Corporation, Japan). The PXRD patterns were recorded with a step size of 0.005° and measurement speed of 5°/min using Cu K alpha radiation.

The porosity of the samples was examined by N_2 adsorption experiments at 77 K using BelsorpMax (MicrotracBEL, Japan). Before the adsorption, the samples were degassed with vacuum at elevated temperatures. MIL-120(Al) and CALF-20 were degassed for 12 h at a relatively low temperature of 150 °C and 110 °C, respectively. Zeolites require higher temperatures to eliminate strongly bonded water molecules. Zeolite 5A was degassed at 320 °C overnight, whereas Zeolite 13X was degassed at 350 °C overnight. BET surface area of the samples was determined using the collected adsorption points within a suitable pressure range selected following previously reported criteria.^{55, 56} Total pore volume was calculated using an adsorption point at the P/P₀ higher than 0.95.

 CO_2 and N_2 adsorption isotherms at cryogenic temperatures were measured using HPVA II (Micromeritics Instrument Corporation, US) with a single-stage cryogenic refrigerator, Cryostat I (Micromeritics Instrument Corporation, US). Multiple CO_2 adsorption experiments under nearcryogenic temperatures were conducted to find the optimum temperature for each sample. For MIL-120(Al), CO_2 adsorption behaviors at 160 K, 180 K, 200 K, and 220 K were observed. The N_2 adsorption isotherm of MIL-120(Al) was collected at 160 K to predict CO_2/N_2 mixture adsorption behavior using ideal adsorbed solution theory (IAST)⁵⁷ at the temperature. Similarly, CO_2 adsorption isotherms at 180 K, 200 K, and 220 K along with an N₂ adsorption isotherm at 220 K were collected at 220 K for Zeolite 5A. For Zeolite 13X, both CO₂ and N₂ adsorption isotherms were collected at 180 K, 200 K, and 220 K to predict CO₂/N₂ mixture adsorption behavior using IAST at the temperatures. For CALF-20, CO₂ adsorption behaviors at 180 K, 195 K, 200 K, and 220 K were observed. The N₂ adsorption isotherm of CALF-20 was collected at 195 K. For Zeolite 13X and CALF-20, several CO₂ adsorption experiments at some temperatures between 273 K and 473 K were conducted to examine suitable desorption conditions. All the IAST predictions were conducted using IAST++ software⁵⁸ by fitting the experimental data with a dual-site Langmuir-Freundlich equation.⁵⁹ All the curve fittings were accomplished with $R^2 > 0.998$.

CO₂ adsorption behavior of Zeolite 13X and CALF-20 was measured using another volumetric apparatus capable of activation under high vacuum, ASAP2020HD analyzer (Micromeritics Instrument Corporation, US) (**Figure S16**). During the adsorption experiment, the cell temperature was maintained at 195 K using a dry ice/acetone cooling bath.

S1.2.4. Breakthrough analysis

Breakthrough analyses on Zeolite 13X and CALF-20 were conducted at 195 K using a custom-built fixed bed system. For both adsorbents, the powder was loosely packed in a 10 cm long, 1/4 inch stainless steel tube. The powder-packed column was installed in a breakthrough system with gas flow controllers and detectors (**Figure S15**). The temperature was maintained around 195 K via a dry ice/ethanol cooling bath. The temperature during all measurements was maintained under 196 K (**Figures S17** and **S18**). To guarantee the dehumidification of feed gas, a bed packed with silica gel was installed before the adsorption bed.

Activation of the Zeolite 13X bed was conducted by raising the temperature to 350 °C under 100 sccm of N_2 flow for 4 h. Similarly, activation of the CALF-20 bed was conducted by raising the temperature to 150 °C under 100 sccm of N_2 flow for 12 h. After the degassing, the system was submerged in a dry ice/ethanol bath. After the bed temperature was stabilized, the inlet gas stream to the bed was switched to 400 ppm CO₂ under N_2 or He balances with a flow rate of 100 sccm or 200 sccm. The outlet gas concentration profile was recorded by LI-850 gas analyzer (LI-COR Biosciences, USA).

The desorption experiment was conducted after recording the CO₂ adsorption experiment with 100 sccm of 400 ppm CO₂ under an N₂ balance. For Zeolite 13X, the bed was purged with 100 sccm of He for 10 min at 195 K. While flowing He at 100 sccm, the bed temperature was first raised to around 20 °C by heating under ambient air. When the bed temperature reached 20 °C, it was further raised to 473 K by heating tape. The mass spectrometer, Pfeiffer Vacuum QMS 200 Omnistar Mass Spectrometer (Pfeiffer Vacuum GmbH, Germany), recorded the outlet gas concentration profile. For CALF-20, the bed was first evacuated at 195 K by vacuum pump, down to ~0.08 bar. While evacuating, the bed was heated by ambient air. The flow rate and concentration of the evacuated gas were recorded by a mass flow meter and LI-850 gas analyzer. After the bed temperature reached ~22 °C, N₂ flowed through the downstream lines to quantify the existing CO₂ inside the lines and vacuum pump. Due to the high fluctuation of flow rates during the last N₂ purging step with vacuuming, the quantification of CO₂ inside the downstream lines can be relatively inaccurate.

To examine the saturation uptake of the Zeolite 13X bed, a breakthrough analysis was conducted using a feed gas stream of 1% (10,000 ppm) CO₂ mixture in N₂ balance at 50 sccm (**Figure S16**). The outlet gas concentration profile was recorded using an LI-850 gas analyzer, after dilution with 100 sccm N₂ flow.

S2. Candidate material selection for near-cryogenic DAC

As mentioned earier, MIL-120(Ga) (UVEXAV)⁴⁸ was selected directly from MC and GCMC simulation results for structures in the CoRE-MOF DDEC database due to its moderate heat of adsorption for CO₂, high Henry's constant at 160 K and 220 K, high CO₂/N₂ selectivity, and high CO₂ uptake at 40 Pa, 220 K (Table S3). However, the number of studies that have synthesized and tested MIL-120(Ga) is small, which raises questions on the reproducibility of its synthesis, especially on a large scale. Instead, its isostructural MOF with more frequent reports, MIL-120(Al) (BUSQIQ)⁴⁹ was included for examination by simulation after point charges were assigned by the DDEC method (**Figure S8**). MIL-120(Al) exhibited a higher Henry's constant for CO₂ adsorption than MIL-120(Ga) under near-cryogenic DAC conditions, and therefore, MIL-120(Al) was selected as the first synthetic target.

Other candidate sorbents were found through relatively indirect routes, using the guideline established from the large-scale molecular simulations. Optimal sorbent physical properties for near-cryogenic DAC were derived from the simulation results as described in the following paragraph (Table S1). The approach enabled us to find sorbent candidates outside of the CoRE-MOF DDEC database.

To derive the optimal conditions for a near-cryogenic DAC sorbent, the physical properties of structures with promising Henry's constant (K_H) at 160 K or 220 K (0.1388 mol kg⁻¹Pa⁻¹ < K_H < 113.2 mol kg⁻¹Pa⁻¹) were analyzed. For eight properties, namely, crystal density, pore volume, largest cavity diameter, pore limiting diameter, gravimetric surface area, volumetric surface area, and helium void fraction, the physical properties between the 1st and 3rd quartile of the MOFs with promising K_H were regarded as indicators for a promising near-cryogenic DAC sorbent.

Notably, these criteria can be useful in finding adsorbents that have suitable interaction with CO₂ at near-cryogenic DAC conditions with a higher likelihood, but they are not necessarily relevant to high CO₂ uptake, since the uptake can be limited by saturation capacity (or pore volume). From this perspective, due to their positive correlation with saturation CO₂ uptake (**Figure S5**), higher pore volume and largest cavity diameter are considered favorable. In the GCMC simulation results, it was shown that CO₂ uptake surpassing what is typically observed under ambient DAC conditions can be achieved under near-cryogenic DAC, especially with structures with $\Delta \hat{H}_s$ ranging from -36 to -60 kJ/mol (**Figure 2D** and **Figure S6**), a pore volume ranging from 0.73 to 1.55 cc/g, and a largest cavity diameter in this region were also regarded as promising for near-cryogenic DAC. The physisorbents that satisfy these conditions were searched, especially among materials known for high CO₂ selectivity.

Zeolite 13X and CALF-20 satisfied seven criteria out of eight (Table S2 and **Figure S7**) and thus were selected for experimental validation. Zeolite 5A was selected as a control experiment material since it satisfied four criteria and is known to have a higher affinity for CO_2 than Zeolite 13X.^{60, 61} All the physisorbents are known to have high CO_2/N_2 selectivity, excellent stability, and low sorbent cost.

S3. Techno-economic analysis of near-cryogenic DAC

A techno-economic analysis (TEA) was conducted for the LNG-DAC process employing Zeolite 13X and CALF-20 as sorbent materials and for temperature vacuum swing adsorption (TVSA) based ambient DAC using amine sorbents. Levelized cost of capture (LCOC) is total annual capital and operational expenditures divided by the CO_2 capture scale, and energy intensity (EI) is total electrical and thermal energy divided by the CO_2 capture scale. LCOC and EI were calculated from the equations below.

$$LCOC (USD tCO_2^{-1}) = \frac{CAPEX_{ann} + OPEX (USD year^{-1})}{M_{DACscale} (tCO_2 year^{-1})}$$
Equation 1
EI (GJ tCO_2^{-1}) = $\frac{Q_{total} + E_{total} (GJ year^{-1})}{M_{DACscale} (tCO_2 year^{-1})}$ Equation 2

S3.1. Energy duty calculations

For Zeolite 13X-based system, CO_2 captured at 195 K from dry air is assumed to be desorbed at 473 K using pure CO_2 as a desorbent gas.⁶² The CO_2 working capacity under the near-cryogenic DAC process was estimated based on the CO_2 uptake measured in the breakthrough experiment and the uptake at 473 K and 1 bar measured in the static adsorption instrument, HPVA II (see S1.2.3.). For the CALF-20 system, CO_2 captured at 195 K from dry air is assumed to be desorbed at 283 K using a vacuum pump. The CO_2 working capacity was estimated based on the CO_2 uptake measured in the breakthrough experiment and the uptake at 283 K and 0.1 bar, as determined by HPVA II measurements. The specific parameter values used for the sorbent are provided in Tables S8 and S9, respectively.

Techno-economic feasibility of amine sorbent-based ambient DAC system was also evaluated, employing operating conditions in previous studies. Adsorption at 298 K from humid air with 400 ppm CO_2 and vacuum-assisted desorption at 383 K were considered. The target vacuum pressure was set to be 0.1 bar. CO_2 working capacities and other parameters used are specified in Table S5–S10.

S3.1.1 Energy duty for cooling & adsorption process

The total cold energy required for the adsorption step was calculated by summing enthalpy changes: Dry air (including CO_2 in the air) cooling, condensing the humidity in the air, adsorbents cooling, and CO_2 adsorption heat (**Figure 5**). In LNG-DAC, all these enthalpy changes were assumed to be achieved by using cold energy from LNG regasification. For LNG-DAC, Feed air was assumed to be humid air with 400 ppm CO_2 at 14 °C (RH=68%), employing the climate conditions of Cove Point, Maryland, USA as a benchmark. The case using an external cooling cycle is addressed in S3.6.

$$E_{cold} = E_{air,c} + E_{humid,c} + E_{ads,c} + E_{hoa,c}$$

Total feed air volume was estimated based on the total CO_2 capture scale (8760 t CO_2 /year) and mass transfer coefficient. The mass transfer coefficient for near-cryogenic adsorption was set to be lower than that of the amine sorbent-based system reflecting the temperature dependence of coefficients. The assumption is conservative, since physisorbents do not have severe internal resistance shown in amine sorbents that is related to amine mobility and reaction (sorption) kinetics, and therefore can have faster overall sorption kinetics even under lower temperatures. The major mass transfer resistance is expected to be intra-particle diffusion, and therefore the temperature dependence of the overall mass transfer coefficient was estimated following that of Knudsen diffusion.

 $k \propto D_k / \delta \propto \sqrt{T}$ (When Knudsen diffusion is dominant)

Equation 4

Equation 3

$$k_{195K}/k_{298K} = \sqrt{195/298} = 0.809$$

Equation 5

Then fan energy was calculated using the following equations.

$$E_{fan} = \frac{1}{\eta_{fan}} \Delta P \times F_{air}$$
 Equation 6

$$F_{air} = A_{cont} \times v_{air}$$
 Equation 7

$$A_{cont} = \left(1 - \exp\left(-\frac{r_{A2V} \times h \times k}{v_{air}}\right)\right)^{-1} \times \frac{M_{DACscale}}{(v_{air} \times C_{CO_2})}$$
Equation 8

S3.1.2 Energy duty for heating & desorption

The thermal energy required for the desorption process was calculated by summing the enthalpy required for desorbing CO₂ (Q_{lat,CO_2}) and the energy required for heating the adsorbent bed ($Q_{sen,ads}$) and the released CO₂ (Q_{sen,CO_2}). Constant specific heat capacity was assumed for the adsorbents (Zeolite 13X, CALF-20, and amine sorbents). The specific heat capacities of CO₂, dry air, and water were assumed to be constant and equal to those of the vapor phase, regardless of whether they are adsorbed or not. CO₂ desorption was assumed to occur linearly with increasing temperature, based on observations of significant desorption at temperatures below 283 K (**Figure 4**). The thermal energy for heating the adsorbent bed from 200 K to 283 K was assumed to be supplied by thermal coupling with seawater. Therefore, the thermal energy required during heating the system from 200 K to 283 K was excluded from the total thermal energy requirements.

For the Zeolite 13X-based LNG-DAC process, the required thermal energy was calculated by summing the latent heats (Q_{lat,CO_2}) and the sensible heats $(Q_{sen,ads}, Q_{sen,CO_2})$ during the heating from 283 K to 473 K.

$$Q_{lat,CO_2} = M_{DACscale} \times \left(\frac{1}{10^3} \times \Delta \widehat{H}_{s,13X,CO_2}\right) \times \frac{T_{des} - T_{h1}}{T_{des} - T_{ads}} \times \frac{1}{(1 - Q_{loss})}$$
Equation 9

$$Q_{sen,CO_2} = M_{DACscale} \times \left(\frac{1}{10^3} \times C_{p,CO_2}\right) \times \left(T_{des} - T_{h1}\right) \times \frac{1}{(1 - Q_{loss})}$$
Equation 10

$$Q_{sen,ads} = N_{cycle} \times M_{ads} \times (\frac{1}{10^6} \times C_{p,13x}) \times (T_{des} - T_{h1}) \times \frac{1}{(1 - Q_{loss})}$$
Equation 11

$$M_{ads} = \frac{10^3 \times M_{DACscale}}{wc \times N_{cycle}}$$
 Equation 12

In contrast, $T_{des} = T_{h1}$ in the CALF-20-based system, which leads to zero thermal energy duty.

In the amine sorbent-based system, the thermal energy duty for the latent and sensible heat of water must be included. Also, M_{ads} needs to be adjusted to account for sorbent degradation. The equations for Q_{sen,CO_2} and $Q_{sen,ads}$ are the same with Equation 10 and Equation 11.

$$Q_{lat,CO_2} = M_{DACscale} \times \left(\frac{1}{10^3} \times \Delta \hat{H}_{s,amine,CO_2}\right) \times \frac{1}{(1 - Q_{loss})}$$
Equation 13

$$Q_{lat,H_20} = M_{DACscale} \times r_{H_20/C0_2} \times (\frac{1}{10^3} \times \Delta \hat{H}_{s,amine,H_20}) \times \frac{1}{(1 - Q_{loss})} \times \frac{1}{(1 - \eta_{lat,rec})}$$
Equation 14

$$Q_{sen,CO_2} = M_{DACscale} \times \left(\frac{1}{10^3} \times C_{p,CO_2}\right) \times \left(T_{des} - T_{ads}\right) \times \frac{1}{(1 - Q_{loss})}$$
Equation 15

$$Q_{sen,ads} = N_{cycle} \times M_{ads} \times (\frac{1}{10^6} \times C_{p,amine}) \times (T_{des} - T_{ads}) \times \frac{1}{(1 - Q_{loss})}$$
Equation 16

$$Q_{sen,H_2O} = M_{DACscale} \times r_{H_2O/CO_2} \times (\frac{1}{10^3} \times C_{p,water}) \times (T_{des} - T_{ads}) \times \frac{1}{(1 - Q_{loss})}$$
Equation 17

$$M_{ads} = \frac{10^3 \times M_{DACscale}}{f_{deg} \times wc \times N_{cycle}}$$
Equation 18

$$f_{deg} = \frac{wc_{act,opt}}{wc} = fun(r_{deg})$$
 Equation 19

The procedure for finding $wc_{act,opt}$ is addressed in a later part (S3.4).

The electrical energy duty for desorption was calculated based on the energy for vacuum pump operation. Since the Zeolite 13X-based system does not use a vacuum pump for desorption, E_{vac,CO_2} was assigned a value of zero. For both the CALF-20-based system and the amine sorbent-based system, the target vacuum pressure was set to 100 mbar.

$$E_{vac,CO_2} = \frac{1}{\eta_{vac}} \times \frac{1}{10^3} \times (\frac{M_{DACscale}}{44}) \times \mathbb{R} \times T_{des} \ln\left(\frac{P_{atm}}{P_{vac}}\right)$$
Equation 20

For the amine sorbent-based system, the energy duty for water evacuation was included.

$$E_{vac,H_2O} = \frac{1}{\eta_{vac}} \times \frac{1}{10^3} \times \left(\frac{M_{DACscale} \times r_{H_2O/CO_2}}{18}\right) \times \mathbb{R} \times T_{des} \ln(r_{comp})$$
Equation 21

S3.2 Operating expenditure (OPEX) estimation

$$OPEX = Q_{total} \times C_{thrm} + E_{total} \times C_{elec} + OPEX_{ads}$$
 Equation 22

$$Q_{total} = \frac{Q_{sum}}{\eta_{thrm}}$$
 Equation 23

$$Q_{sum} = Q_{sen,CO_2} + Q_{sen,H_2O} + Q_{sen,ads} + Q_{lat,CO_2} + Q_{lat,H_2O}$$
Equation 24

$$E_{total} = \frac{E_{sum}}{\eta_{elec}}$$
 Equation 25

$$E_{sum} = E_{fan} + E_{vac,CO_2} + E_{vac,H_2O}$$
Equation 26

For Zeolite 13X and CALF-20, $OPEX_{ads} \approx 0$, assuming negligible degradation of the sorbents. For amine sorbents, $OPEX_{ads}$ is a function of sorbent price (C_{ads}) and sorbent replacement period (y_{MU}). The M_{ads} and y_{MU} were determined based on r_{deg} , which is addressed in S3.4.

$OPEX_{ads} = \frac{M_{ads}}{y_{MU,opt}} \times C_{ads} \times f_{ads}$	Equation 27
$y_{MU} = fun(r_{deg})$	Equation 28
$M_{ads} = fun(r_{deg})$	Equation 29

S3.3 Capital expenditure (CAPEX) estimation

The CAPEX of near-cryogenic DAC systems and an ambient DAC system was estimated using the equations below. Among the parameters used, the derivations of A_{he} , total, M_{ads} , and $CAPEX_{cont}$ are detailed in S3.4 and S3.5.

$$C_{fan} = \left(\frac{F_{air}}{F_{air,ref}}\right)^{0.8} \times C_{fan,ref}$$
Equation 30

$$C_{vac} = (a_{coef} \times (\dot{F}_{vac})^{b_{coef}} + c_{coef}) \times 1.07$$
 Equation 31

$$\dot{F}_{vac} = \frac{10^6 \times M_{DACscale} \times \left(\frac{1}{44} + \frac{r_{H_2O/CO_2}}{18}\right) \times 8.314 \times T_{des}}{10^2 \times P_{atm}} \times \frac{1}{365 \times 24}$$
 Equation 32

$$C_{hex} = 2 \times (A_{hex,total})^{0.7} \times C_{hex,area}$$
 Equation 33

$$C_{equip} = C_{fan} + C_{vac} + C_{hex}$$
Equation 34

$$CAPEX = CAPEX_{equip} + CAPEX_{bed}$$
 Equation 35

$$CAPEX_{equip} = C_{equip} \times f_{TCI}$$
 Equation 36

$$CAPEX_{bed} = CAPEX_{ads} + CAPEX_{cont}$$
 Equation 37

$$CAPEX_{ads} = M_{ads} \times C_{ads} \times f_{ads}$$
Equation 38

$$CAPEX_{ann} = CAPEX \times f_{ann}$$
 Equation 39

$$f_{ann} = IR \times \left(1 - \frac{1}{(1 + IR)^{\gamma} f}\right)^{-1}$$
 Equation 40

S3.4 Sorbent cost (OPEX_{ads} and CAPEX_{ads}) estimation

The degradation of amine sorbents was modeled by a simple exponential function.

$$wc_{act} = fun(y) = wc \times e^{-c \cdot y}$$
Equation 41
Since $wc_{act}(y = 1) = wc \times e^{-c} = wc \times (\frac{100 - r_{deg}}{100}),$

$$c = -\ln\left(\frac{100 - r_{deg}}{100}\right)$$
Equation 42

The average working capacity during operation before sorbent replacement period (y_{MU}) was then calculated using Equation 43 and Equation 44.

$$wc_{act,aver} = \frac{1}{y_{MU}} \int_{y=0}^{y=y_{MU}} wc_{act} \, dy = \frac{wc}{y_{MU}} \int_{y=0}^{y=y_{MU}} e^{-c \cdot y} \, dy = \frac{wc}{-c \cdot y_{MU}} \times (1 - e^{-c \cdot y_{MU}})$$
Equation 43
$$M_{ads} = \frac{10^3 \times M_{DACscale}}{wc_{act,aver} \times N_{cycle}}$$
Equation 44

The LCOC contribution of sorbent costs ($OPEX_{ads}$ and $CAPEX_{ads,ann}$) was calculated for various y_{MU} values (**Figure S24**). The optimal replacement period ($y_{MU,opt}$) and the average CO₂ working capacity under the optimal replacement ($wc_{act,opt}$) were determined when the sum of sorbent costs was minimized. Using Equation 43 and Equation 19, M_{ads} and f_{deg} were calculated.

Contactor capital costs were derived from C_{cont} as shown below.

$CAPEX_{cont} = M_{ads} \times C_{cont} \times f_{cont}$	Equation 45
--	-------------

All parameters used are given in Tables S5-S10.

Each component of CAPEX can be represented in its annualized value as shown below.

$CAPEX_{fan,ann} = CAPEX_{fan} \times f_{ann}$	Equation 46
$CAPEX_{vac,ann} = CAPEX_{vac} \times f_{ann}$	Equation 47
$CAPEX_{hex,ann} = CAPEX_{he} \times f_{ann}$	Equation 48
$CAPEX_{bed,ann} = CAPEX_{bed} \times f_{ann}$	Equation 49

S3.5. Additional heat exchanger area estimation (LNG-DAC)

While the LNG-DAC process provides significant benefits, there is a potential drawback related to inefficiency in heat exchange for LNG regasification, which may result in a considerable increase in the required heat exchanger surface area and capital costs. The additional cost for the heat exchanger in the LNG-DAC process was estimated by comparing it to that of conventional open rack vaporizer (ORV)¹⁰ and ambient air vaporizer (AAV).^{8,9} ORV offers fast heat transfer by regasifying LNG through heat exchange with seawater. In contrast, AAV regasifies LNG through heat exchange with ambient air to avoid any negative environmental impact stemming from the outlet cold water of ORV. However, the use of air instead of water results in less efficient heat transfer due to lower convection heat transfer coefficient of air.

In the LNG-DAC process, the LNG is initially regasified through heat exchange with the air, similar to the AAV approach, resulting in NG at a specific temperature ($T_{NG,1}$). The NG is then further heated to near-room temperature (~283 K) through heat exchange with seawater, similar to the ORV.

The heat exchanger for LNG-DAC coupling was assumed to have a similar overall heat transfer coefficient as that of AAV. The initial condition of LNG was assumed to be 1 bar and 109.1 K. LNG regasification, coupled with DAC, produces NG at $T_{NG,1}$ and 1 bar. LNG evaporation enthalpy $(\Delta \hat{H}_{NG,evap})$, energy for heating the NG to $T_{NG,1}$ ($\Delta \hat{H}_{heati}_{,1}$), and energy for heating the NG from $T_{NG,1}$ to 283 K ($\Delta \hat{H}_{heati}_{,2}$) were derived from the NIST web book, assuming NG composed of methane (90%) and ethane (10%). The overall heat transfer coefficient was obtained from previous literature for AAV and ORV. The heat exchanger area for LNG-DAC (**Figure S25**) was calculated using the following equations.

$$Q_{reg,total} = Q_{evap} + Q_{heating,1} = \Delta \hat{H}_{NG,evap} \cdot \dot{m}_{LNG} + \Delta \hat{H}_{heating,1} \cdot \dot{m}_{LNG}$$
Equation 50

$$Q_{evap} = A_{evap} \cdot U_{evap,air} \cdot LMTD$$
 Equation 51

$$Q_{heating,1} = A_{heating,1} \cdot U_{heating,air} \cdot LMTD$$
 Equation 52

 $Q_{heating,2} = A_{heating,2} \cdot U_{heating,water} \cdot LMTD$ Equation 53

 $A_{hex,total} = A_{evap} + A_{heating,1} + A_{heating,2}$ Equation 54

where $Q_{reg,total}$ is the amount of heat required for natural gas regasification in the LNG-DAC system, which is equal to the amount of cold energy for operating a DAC system (1kg Zeolite 13X, 1 cycle/h). LMTD represents the logarithmic average of the temperature difference. All parameters used for the calculation are provided in **Tables S5** and **S6**.

Although the overall heat transfer coefficient was assumed to be equal, the heat transfer between LNG/NG and air can be relatively inefficient in the LNG-DAC heat exchanger compared to AAV due

to a smaller LMTD. In contrast, NG heating from $T_{NG,1}$ to 283 K in LNG-DAC coupling is expected to be more efficient than AAV, owing to the much higher convection heat transfer coefficient on the water side. As a result, LNG-DAC does not require additional heat exchanger area compared to AAV when $T_{NG,1}$ is set at temperatures lower than 263 K (**Figure S25**). Even when seawater is not involved in NG heating ($T_{NG,1}$ =283 K), the total heat exchanger area required for LNG-DAC coupling is expected to be only 25% larger than that of AAV.

On the other hand, the LNG-DAC coupling requires a significantly larger heat transfer area compared to the ORV. That being said, the additional heat exchanger cost was estimated to be trivial compared to the expected profits from CO₂ production (**Figure S26**). The additional heat exchanger cost could be reduced by lowering $T_{NG,1}$; however, the cost savings achieved by lowering $T_{NG,1}$ were not significant. Therefore, reducing $T_{NG,1}$ at the expense of increased LNG consumption is not expected to be worthwhile (**Figure S27**).

The heat exchanger area and cost of the LNG-DAC process with cold energy recovery from downstream air were estimated in a similar manner. The heat transfer between cold air and fresh warm air was calculated using the overall heat transfer coefficient of the air-air heat exchanger from the literature.³⁻⁵ The mass flow rates of cold downstream air and warm fresh air were assumed to be equal. The total additional heat exchanger area and costs, including the air-air heat exchanger, were estimated under various cold energy (or enthalpy) recovery efficiencies.

$$A_{hex,total} = A_{air-air} + A_{evap} + A_{heating,1} + A_{heating,2}$$
Equation 55
$$A_{air-air} = \frac{Q_{air-air}}{U_{air-air} \cdot LMTD}$$
Equation 56
$$Q_{air-air} = E_{air,c} \times \eta_{c,rec}$$
Equation 57

S3.6. Global LNG-DAC potential estimation

The annual global regasification capacity (M_{LNG}) was estimated based on a scenario where it increases proportionally with the growth in global LNG trades (imports), following the trend predicted by the U.S. Energy Information Administration (International Energy Outlook 2023).³¹

The global LNG-DAC potential (M_{CO2}) was calculated using the following equations.

$$\left(\frac{\Delta \hat{H}_{NG,evap} + \Delta \hat{H}_{heating,1}}{10^3}\right) \cdot \dot{m}_{LNG} = E_{cold} \cdot \dot{m}_{CO_2}$$
 Equation 58

$$M_{CO_2} = \frac{\dot{m}_{CO_2}}{\dot{m}_{LNG}} \cdot M_{LNG}$$
 Equation 59

where \dot{m}_{CO_2} is CO₂ captured by operating a DAC system and \dot{m}_{LNG} is the consumption of LNG.

The effect of the adsorption temperature of the LNG-DAC process on $\dot{m}_{CO_2}/\dot{m}_{LNG}$ was estimated by adjusting the enthalpy required for cooling the feed air (Figure S31). On the other hand, the effect of capture efficiency (η_{cap}) was estimated considering the decrease in the total amount of feed air to be cooled and the amount of moisture to be condensed (Figure S30).

As mentioned earlier in S3.5, the cold energy of downstream air can be recovered using an air-air heat exchanger and utilized to cool fresh feed air (**Figure S28a**). Cold energy recovery can significantly decrease E_{cold} by reducing $E_{air,c}$. Considering cold energy recovery, the actual cold energy required for air cooling ($E_{air,c,act}$) decreases based on the cold energy recovery efficiency ($\eta_{c,rec}$).

 $E_{air,c,act} = E_{air,c} \cdot (1 - \eta_{c,rec})$

The effect of integrating natural gas combustion with LNG-DAC (**Figure S28b**) was estimated by considering the decrease in the total amount of feed air to be cooled and the amount of moisture to be condensed. The amount of CO_2 added to the feed air was calculated using the CO_2 emission per unit of natural gas energy (56 kgCO₂/GJ)⁷ and the thermal energy required for desorption.

S3.7. Energy estimation for external cooling cycle-based system

Compressor work input to cool air for direct desublimation of CO_2 and for operating near-cryogenic DAC was estimated (**Figure S33**) under four cold ambient environments: Snag, Yukon (5 °C); Oymyakon, Russia (-15 °C); and Vostok Station, Antarctica (-40 and -65 °C). All procedures for calculating the compressor work followed methods outlined in the literature.^{29, 30} Radiation cooling with the night sky was assumed at 25 °C.

Direct desublimation has a limitation in capture efficiency (η_{cap}) when utilizing a high-efficiency precooler (or cold energy recovery heat exchanger) due to fouling caused by solidified CO₂ within the heat exchanger. Maximum η_{cap} when using a precooler with $\eta_{c,rec} = 0.9$ and 0.95, was assumed to be 0.4 and 0.6, respectively, based on previous studies. When $\eta_{c,rec}$ is lower than 0.9, such a limitation in η_{cap} was not considered. Under each condition, the optimal η_{cap} that minimizes work input was selected. Near-cryogenic DAC is expected to be free from such fouling issues due to its much higher operation temperatures compared to CO₂ desublimation temperatures. In both cases, only the compressor work for dry air cooling was considered. The detailed procedure for the estimation can be found in the literature.

The feasibility of external cooling cycles for near-cryogenic DAC was also assessed. As discussed earlier, cooling atmospheric air in warm regions (>15 °C) to near-cryogenic temperatures is deemed impractical (**Figure S23**). The selection of regional DAC points under cold climates and systematic manners to minimize cold energy consumption were guided by previous research on the direct sublimation of atmospheric CO_2 .^{29, 30} Results indicate that the input work for air cooling in near-cryogenic DAC (0–9.0 GJ/tCO₂) is significantly lower than that required for direct sublimation (45.8–163.2 GJ/tCO₂) (**Figure S33**). The additional energy cost of operating cooling loops for near-cryogenic DAC is estimated to range from 0 to 37.0 USD/tCO₂, depending on atmospheric temperatures ranging from -65 °C to -15 °C.

Reference

- 1. X. Shao, Q. Deng, M. Jiang and Q. Chen, *Processes*, 2022, **10**, 2521.
- E. W. Lemmon, I. H. Bell, M. L. Huber and M. O. McLinden, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, ch. Thermophysical Properties of Fluid Systems.
- 3. H. S. Dizaji, S. Pourhedayat, H. Moria, S. Alqahtani, S. Alshehery and A. E. Anqi, *Energy*, 2024, **290**, 130037.
- T. Jan, O. Paweł, T. Dawid and N.-O. Marzena, in *Heat Transfer Studies and Applications*, ed. K. Salim Newaz, IntechOpen, London, 2015, ch. 10. Computer-Aided Determination of the Air-Side Heat Transfer Coefficient and Thermal Contact Resistance for a Fin-and-Tube Heat Exchanger.
- 5. The Engineering ToolBox, https://www.engineeringtoolbox.com/heat-transfer-coefficients-exchangersd_450.html, (accessed February, 2025).
- K. Rennert, F. Errickson, B. C. Prest, L. Rennels, R. G. Newell, W. Pizer, C. Kingdon, J. Wingenroth, R. Cooke, B. Parthum, D. Smith, K. Cromar, D. Diaz, F. C. Moore, U. K. Müller, R. J. Plevin, A. E. Raftery, H. Ševčíková, H. Sheets, J. H. Stock, T. Tan, M. Watson, T. E. Wong and D. Anthoff, *Nature*, 2022, 610, 687-692.
- 7. T. Simmons, *CO*₂ *Emissions from Stationary Combustion of Fossil Fuels*, Intergovernmental Panel on Climate Change (IPCC), 2001.
- 8. J. Wang, C. Li, W. Jia and K. Wang, *Processes*, 2022, 10, 851.
- 9. G. Ma, C. Zhang and L. Zhao, *Adv. Mech. Eng.*, 2017, **9**, 1687814017711856.
- 10. K. Huang, X. Zhou, C. Huang, L. Wang, D. Li and J. Zhao, *Energies*, 2023, 16, 1383.
- 11. E. Cao, Heat Transfer in Process Engineering, McGraw-Hill Education, New York, 2010.
- 12. H. Afrianto, M. R. Tanshen, B. Munkhbayar, U. Tony Suryo, H. Chung and H. Jeong, *Int. J. Heat Mass Transf.*, 2014, **68**, 110-118.
- 13. Y. Miao, Z. He, X. Zhu, D. Izikowitz and J. Li, Chem. Eng. J., 2021, 426, 131875.
- 14. A. Ahmadian Hosseini and M. Jahandar Lashaki, Sep. Purif. Technol., 2023, 325, 124580.
- 15. W. Zhang, H. Liu, C. Sun, T. C. Drage and C. E. Snape, *Chem. Eng. J.*, 2014, **251**, 293-303.
- 16. D. Panda, V. Kulkarni and S. K. Singh, *React. Chem. Eng.*, 2023, **8**, 10-40.
- 17. G. Rim, P. Priyadarshini, M. Song, Y. Wang, A. Bai, M. J. Realff, R. P. Lively and C. W. Jones, *J. Am. Chem. Soc.*, 2023, **145**, 7190-7204.
- 18. H. E. Holmes, S. Banerjee, A. Vallace, R. P. Lively, C. W. Jones and M. J. Realff, *Energy Environ. Sci.*, 2024, **17**, 4544-4559.
- 19. J. Kim, S. Jamdade, Y. Yuan and M. J. Realff, *Energy*, 2024, **299**, 131376.
- 20. E. Scuiller, P. Dutournié, M. Zbair and S. Bennici, J. Chem. Eng. Data, 2023, 68, 1865-1871.
- 21. K. N. Son, G. E. Cmarik, J. C. Knox, J. A. Weibel and S. V. Garimella, *J. Chem. Eng. Data*, 2018, **63**, 1663-1674.
- 22. Global Cement Magazine, https://www.globalcement.com/magazine/articles/1194-lafargeholcim-and-svante-preparing-for-the-future-carbon-economy, (accessed February, 2025).
- 23. J. Kim, Y. Yuan, Y. Ren, B. A. McCool, R. P. Lively and M. J. Realff, *Energy Convers. Manage.*, 2024, **319**, 118877.
- 24. Businessinsider, https://markets.businessinsider.com/commodities/natural-gas-price, (accessed February, 2025).
- 25. A. Sinha, L. A. Darunte, C. W. Jones, M. J. Realff and Y. Kawajiri, *Ind. Eng. Chem. Res.*, 2017, **56**, 750-764.
- V. K. Patel, V. J. Savsani and M. A. Tawhid, in *Thermal System Optimization: A Population-Based Metaheuristic Approach*, eds. V. K. Patel, V. J. Savsani and M. A. Tawhid, Springer, Cham, 2019, ch. Thermal Design and Optimization of Heat Exchangers, pp. 33-98.
- 27. J. Kim, S. S. Han, J. Kim, I.-B. Lee, H. Oh and Y.-S. Yoon, *Energy*, 2023, 264, 126281.
- 28. J. Kim, J. Kim, H. Oh, S. Lee, I.-B. Lee and Y.-S. Yoon, *Energy*, 2022, 241, 122908.
- 29. S. K. S. Boetcher, J. B. Perskin, Y. Maidenberg, M. J. Traum and T. von Hippel, *Carbon Capture Sci. Technol.*, 2023, **8**, 100127.
- 30. S. K. S. Boetcher, M. J. Traum and T. von Hippel, *Clim. Change*, 2020, 158, 517-530.
- 31. U.S. Energy Information Administration, *International Energy Outlook 2023*, 2023.
- 32. S. Alvik, *Hydrogen forecast to 2050*, DNV AS, 2022.
- 33. D. Nazarian, J. S. Camp and D. S. Sholl, *Chem. Mat.*, 2016, 28, 785-793.
- Y. G. Chung, J. Camp, M. Haranczyk, B. J. Sikora, W. Bury, V. Krungleviciute, T. Yildirim, O. K. Farha, D. S. Sholl and R. Q. Snurr, *Chem. Mat.*, 2014, 26, 6185-6192.
- 35. T. A. Manz and D. S. Sholl, J. Chem. Theory Comput., 2010, 6, 2455-2468.

- 36. J. M. Findley and D. S. Sholl, J. Phys. Chem. C, 2021, **125**, 24630-24639.
- 37. T. F. Willems, C. H. Rycroft, M. Kazi, J. C. Meza and M. Haranczyk, *Microporous Mesoporous Mat.*, 2012, **149**, 134-141.
- 38. D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, *Mol. Simul.*, 2016, **42**, 81-101.
- A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, III and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, 114, 10024-10035.
- 40. J. J. Potoff and J. I. Siepmann, *AICHE J.*, 2001, **47**, 1676-1682.
- 41. R. Babarao and J. Jiang, *Langmuir*, 2008, **24**, 5474-5484.
- 42. X. Deng, W. Yang, S. Li, H. Liang, Z. Shi and Z. Qiao, *Appl. Sci.-Basel*, 2020, 10, 569.
- 43. S. Li, Y. G. Chung and R. Q. Snurr, *Langmuir*, 2016, **32**, 10368-10376.
- 44. E. Moubarak, S. M. Moosavi, C. Charalambous, S. Garcia and B. Smit, *Ind. Eng. Chem. Res.*, 2023, **62**, 10252-10265.
- 45. I. B. Orhan, T. C. Le, R. Babarao and A. W. Thornton, Comm. Chem., 2023, 6, 214.
- 46. Z. Qiao, Q. Xu and J. Jiang, J. Membr. Sci., 2018, 551, 47-54.
- 47. W. Yang, H. Liang, F. Peng, Z. Liu, J. Liu and Z. Qiao, *Nanomaterials*, 2019, 9, 467.
- 48. R. Hajjar, C. Volkringer, T. Loiseau, N. Guillou, J. Marrot, G. Férey, I. Margiolaki, G. Fink, C. Morais and F. Taulelle, *Chem. Mat.*, 2011, **23**, 39-47.
- C. Volkringer, T. Loiseau, M. Haouas, F. Taulelle, D. Popov, M. Burghammer, C. Riekel, C. Zlotea, F. Cuevas, M. Latroche, D. Phanon, C. Knöfelv, P. L. Llewellyn and G. Férey, *Chem. Mat.*, 2009, 21, 5783-5791.
- Y. G. Chung, E. Haldoupis, B. J. Bucior, M. Haranczyk, S. Lee, H. Zhang, K. D. Vogiatzis, M. Milisavljevic, S. Ling, J. S. Camp, B. Slater, J. I. Siepmann, D. S. Sholl and R. Q. Snurr, *J. Chem. Eng. Data*, 2019, 64, 5985-5998.
- 51. H. Fang, A. S. S. Daou, S. E. Boulfelfel, J. M. Findley, P. I. Ravikovitch and D. S. Sholl, *J. Phys. Chem. C*, 2023, **127**, 23941-23955.
- 52. W. Loewenstein, Am. Mineral., 1954, **39**, 92-96.
- 53. J.-B. Lin, T. T. Nguyen, R. Vaidhyanathan, J. Burner, J. M. Taylor, H. Durekova, F. Akhtar, R. K. Mah, O. Ghaffari-Nik, S. Marx, N. Fylstra, S. S. Iremonger, K. W. Dawson, P. Sarkar, P. Hovington, A. Rajendran, T. K. Woo and G. K. H. Shimizu, *Science*, 2021, **374**, 1464-1469.
- 54. F. Raganati, M. Bellusci, F. Leardi, F. Varsano and P. Ammendola, *Chem. Eng. J.*, 2025, **506**, 159966.
- 55. F. Ambroz, T. J. Macdonald, V. Martis and I. P. Parkin, *Small Methods*, 2018, **2**, 1800173.
- 56. J. Rouquerol, P. L. Llewellyn and F. Rouquerol, in *Characterization of Porous Solids VII*, eds. P. L. Llewellyn, F. Rodriquez-Reinoso, J. Rouqerol and N. Seaton, Elsevier, Amsterdam, 2007, ch. Is the bet equation applicable to microporous adsorbents?, pp. 49-56.
- 57. A. L. Myers and J. M. Prausnitz, AICHE J., 1965, 11, 121-127.
- 58. S. Lee, J. H. Lee and J. Kim, *Korean J. Chem. Eng.*, 2018, **35**, 214-221.
- 59. X. Tang, N. Ripepi, N. P. Stadie, L. Yu and M. R. Hall, *Fuel*, 2016, **185**, 10-17.
- 60. Q. H. Dirar and K. F. Loughlin, *Adsorption*, 2013, **19**, 1149-1163.
- 61. J. Merel, M. Clausse and F. Meunier, Ind. Eng. Chem. Res., 2008, 47, 209-215.
- 62. M. Song, G. Rim, F. Kong, P. Priyadarshini, C. Rosu, R. P. Lively and C. W. Jones, *Ind. Eng. Chem. Res.*, 2022, **61**, 13624-13634.