DIRECT AIR CAPTURE APPARATUS AND PROCESS AND SYSTEMS FOR THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/568,752, filed on 22 March 2024, the entire contents and substance of which is incorporated herein by reference in its entirety as if fully set forth below.

FIELD OF THE DISCLOSURE

[0002] The present disclosure relates generally to direct air capture (DAC) apparatuses and processes for the capture of CO_2. Particularly, the present disclosure relates to DAC apparatuses and processes for precooled feed lines for the capture of CO_2 and sorbent materials to achieve the same.

BACKGROUND

[0003] Direct air capture of CO_2 (DAC) is a key component of many of the climate scenarios in which global surface temperatures are stabilized within +1.5-2.0 °C relative to pre-industrial times. Despite promising candidate processes and materials for DAC developed over the last decade, the high capital and energy costs of DAC has limited its deployment to date.

[0004] The energy required to recover captured CO_2 during DAC as a purified product is a significant issue. Solid adsorbents, such as amine-impregnated porous oxides, are among the lowest overall energy requirements for DAC processes, with lower-bound estimates for total energy penalty ranging from 4-6 GJ per tonne of CO_2 (tCO_2), although energies in excess of 7 GJ/tCO_2 are commonly realized in practice. Moreover, DAC also requires large capital costs, which largely depend on the performance of sorbent materials, including the working capacity but also the adsorption kinetics, long-term stability, and their price. Unfortunately, the most promising DAC sorbents to date, supported amine sorbents, have limitations in working capacity (~2.5 $mmol/g_{powder}$), adsorption kinetics, and oxidative stability. Moreover, most DAC sorbent materials

also adsorb significant quantities of water from ambient air, and water removal or desorption is often a major energy penalty.

[0005] Recently metal–organic frameworks (MOFs) selected for physisorption-based DAC processes have gathered interest due to favorable adsorption kinetics and low CO_2 desorption enthalpies. A handful of physisorbing MOFs out of the ~60,000 experimentally synthesized MOF materials have been suggested as having sufficient CO_2 affinity for DAC. However, these materials significantly underperformed amine-based materials in realistic DAC experiments, largely due to issues associated with water co-adsorption. In addition, MOFs often require expensive precursors and to date only a very small selection of MOFs have been scaled up. Recent work showed that commercially available zeolites could exhibit moderate DAC performance at sub-ambient temperatures (-20 °C to 0 °C); however, they require a separate water removal process and do not have CO_2 working capacity advantages over amine sorbents operating at ambient conditions and without water removal. The DAC sorption capacity of zeolites was further evaluated at a much lower temperature of -58 °C, where atmospheric air can be assumed to be nearly dry. However, even under these extremely low-temperature conditions, which are naturally achievable but limited to very specific regions and seasons, the sorption capacity of zeolites did not surpass that of conventional amine sorbents.

[0006] DAC at lower temperatures, unattainable for atmospheric air under natural conditions, can fully utilize the capacity of adsorbents with low heats of adsorption for CO_2. Atmospheric air cooling to 120–150 K to directly sublime atmospheric CO_2 ('cryogenic DAC') was found to be infeasible due to the substantial energy required for cooling. Compared to direct sublimation, however, physisorption can facilitate DAC at higher near-cryogenic temperatures (160–240 K), significantly reducing air cooling enthalpy and the CAPEX associated with specialized cryogenic equipment. Nevertheless, it remains essential to leverage free sources of cold energy (e.g., energy recovery) to universally deploy 'near-cryogenic DAC' in warmer regions and extend its broader impact.

[0007] What is needed, therefore, is an improved system and process for DAC that can take advantage of sources of cold energy to deploy near-cryogenic DAC. MOFs and commercially available zeolites further require alterations to achieve improved DAC performance at sub-ambient temperatures. The present disclosure addresses this need as well as other needs as will become apparent upon reading the present disclosure.

BRIEF SUMMARY

[0008] An embodiment of the present disclosure provides a direct air capture (DAC) apparatus. The DAC apparatus comprises a sorbent bed comprising a sorbent material, the sorbent bed operating at a temperature from 160 K to 240 K and a feed line connected to the sorbent bed, the feed line configured to provide a fluid to contact the sorbent material, the fluid comprising CO_2, wherein the sorbent material is configured to adsorb the CO_2 from the fluid when the fluid is in contact with the sorbent material. The sorbent material is defined by a crystal density from 0.2 to 2 g/cm^3, a largest cavity diameter from 4 to 16 Å, and a total pore volume from 0.2 to 1.5 cm^3/g.

[0009] In any of the embodiments disclosed herein, the sorbent material can have a heat of adsorption of 60 kJ/mol or less.

[0010] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

[0011] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

[0012] In any of the embodiments disclosed herein, the sorbent material can have a CO_2 / N_2 selectivity of 4×10^5 or greater measured at a temperature from 160 K to 240 K.

[0013] In any of the embodiments disclosed herein, the fluid in the feed line can be precooled prior to contacting the sorbent material to reach the operating temperature from 160 K to 240 K.

[0014] In any of the embodiments disclosed herein, the DAC apparatus can further comprise a heat exchanger connected to the feed line, the heat exchanger configured to receive liquefied natural gas and conduct a heat exchange between the liquefied natural gas and the fluid in the feed line to precool the fluid in the feed line prior to contacting the sorbent material.

[0015] In any of the embodiments disclosed herein, the liquefied natural gas can exchange heat with the fluid through the heat exchanger while undergoing a regasification process.

[0016] In any of the embodiments disclosed herein, the DAC apparatus can further comprise a desorption line connected to the sorbent bed, the desorption line configured to remove CO_2 from the sorbent bed that has been desorbed from the sorbent material.

[0017] In any of the embodiments disclosed herein, the sorbent bed can be configured to undergo a desorption process operating at from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material to the desorption line.

[0018] In any of the embodiments disclosed herein, the sorbent bed can be configured to undergo a desorption process operating at from 393 K to 623 K and from 0.5 bar to 1.2 bar to release the CO_2 from the sorbent material to the desorption line, and the desorption process comprises contacting the sorbent bed with a purging gas.

[0019] Another embodiment of the present disclosure provides a direct air capture (DAC) system. The DAC system comprises a sorbent bed comprising a sorbent material, the sorbent bed operating at a temperature from 160 K to 240 K, a heat exchanger configured to receive a second fluid and conduct a heat exchange between the second fluid and a first fluid in order to precool the first fluid prior to contacting the sorbent material, and a feed line connecting the heat exchanger and the sorbent bed and configured to transport the first fluid from the heat exchanger to the sorbent bed, wherein the first fluid comprises CO_2, and the sorbent material is configured to adsorb the CO_2 from the first fluid when the first fluid is in contact with the sorbent material. The sorbent material is defined by a crystal density from 0.2 to 2 g/cm^3, a largest cavity diameter from 4 to 16 Å, and a total pore volume from 0.2 to 1.5 cm^3/g.

[0020] In any of the embodiments disclosed herein, the sorbent material can have a heat of adsorption of 60 kJ/mol or less.

[0021] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

[0022] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

[0023] In any of the embodiments disclosed herein, the sorbent material can have a CO_2 / N_2 selectivity of 4×10^5 or greater measured at a temperature from 160 K to 240 K.

[0024] In any of the embodiments disclosed herein, the second fluid can be liquified natural gas.

[0025] In any of the embodiments disclosed herein, the liquefied natural gas can exchange heat with the fluid through the heat exchanger while undergoing a regasification process.

[0026] In any of the embodiments disclosed herein, the DAC apparatus can further comprise a desorption line connected to the sorbent bed, the desorption line configured to remove CO_2 from the sorbent bed that has been desorbed from the sorbent material.

[0027] In any of the embodiments disclosed herein, the sorbent bed can be configured to undergo a desorption process operating at from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material to the desorption line.

[0028] In any of the embodiments disclosed herein, the sorbent bed can be configured to undergo a desorption process operating at from 393 K to 623 K and from 0.5 bar to 1.2 bar to release the CO_2 from the sorbent material to the desorption line, and the desorption process comprises contacting the sorbent bed with a purging gas.

[0029] Another embodiment of the present disclosure provides a direct air capture (DAC) process. The DAC process comprises conducting a heat exchange between a fluid and liquefied natural gas, the liquefied natural gas having a temperature between 100 K and 190 K; contacting the fluid with a sorbent material, the fluid being at a temperature from 160 K to 240 K, the fluid comprising CO_2; and adsorbing the CO_2 from the fluid into the sorbent material. The sorbent material is defined by a crystal density from 0.2 to 2 g/cm^3, a largest cavity diameter from 4 to 16 Å, and a total pore volume from 0.2 to 1.5 cm^3/g.

[0030] In any of the embodiments disclosed herein, the sorbent material can have a heat of adsorption of 60 kJ/mol or less.

[0031] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

[0032] In any of the embodiments disclosed herein, the sorbent material can have a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

[0033] In any of the embodiments disclosed herein, the sorbent material can have a CO_2 / N_2 selectivity of 4 x 10^5 or greater measured at a temperature from 160 K to 240 K.

[0034] In any of the embodiments disclosed herein, the DAC process can further comprise desorbing the CO_2 from the sorbent material, wherein the desorbing occurs from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material.

[0035] In any of the embodiments disclosed herein, the DAC process can further comprise desorbing the CO_2 from the sorbent material, wherein the desorbing occurs from 393 K to 623 K and from 0.5 bar to 1.2 bar to release the CO_2 from the sorbent material.

[0036] In any of the embodiments disclosed herein, the desorbing can further comprise contacting the sorbent bed with a purging gas, and wherein the purging gas comprises high-purity CO_2.

[0037] These and other aspects of the present invention are described in the Detailed Description of the Invention below and the accompanying figures. Other aspects and features of embodiments of the present invention will become apparent to those of ordinary skill in the art upon reviewing the following description of specific, exemplary embodiments of the present invention in concert

with the figures. While features of the present invention may be discussed relative to certain embodiments and figures, all embodiments of the present invention can include one or more of the features discussed herein. Further, while one or more embodiments may be discussed as having certain advantageous features, one or more of such features may also be used with the various embodiments of the invention discussed herein. In similar fashion, while exemplary embodiments may be discussed below as device, system, or method embodiments, it is to be understood that such exemplary embodiments can be implemented in various devices, systems, and methods of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate multiple embodiments of the presently disclosed subject matter and serve to explain the principles of the presently disclosed subject matter. The drawings are not intended to limit the scope of the presently disclosed subject matter in any manner.

[0039] FIG. 1 is a schematic diagram of a direct air capture (DAC) system in accordance with the present disclosure.

[0040] FIG. 2 is a schematic diagram of a direct air capture (DAC) apparatus in accordance with the present disclosure.

[0041] FIG. 3 is a flowchart depicting a direct air capture (DAC) process in accordance with the present disclosure.

[0042] FIGs. 4A–C illustrate an example adsorption and desorption process for a sorbent bed in accordance with the present disclosure.

[0043] FIGs. 5A & 5B are charts of isotherms and adsorption-desorption conditions in accordance with some examples of the present disclosure.

[0044] FIG. 6 is a chart illustrating the effect of temperature on heats of adsorption and Henry's constant in accordance with some examples of the present disclosure.

[0045] FIG. 7 shows violin plots of physical properties for adsorbents with suitable properties in accordance with the present disclosure.

[0046] FIG. 8A shows uptakes of some example sorbent materials and FIG. 8B shows selectivity and uptake of some example sorbent materials in accordance with the present disclosure.

[0047] FIG. 9 is a chart illustrating adsorption isotherms of some example sorbent materials in accordance with the present disclosure.

[0048] FIGs. 10A & 10B are charts of adsorption isotherms for example sorbent materials in accordance with the present disclosure.

[0049] FIGs. 11A–C are charts showing breakthrough curves, adsorption kinetics, and desorption profile of an example sorbent material in accordance with the present disclosure.

[0050] FIGs. 12A–C are charts showing breakthrough curves, adsorption kinetics, and desorption profile of another example sorbent material in accordance with the present disclosure.

DETAILED DESCRIPTION

[0051] Although certain embodiments of the disclosure are explained in detail, it is to be understood that other embodiments are contemplated. Accordingly, it is not intended that the disclosure is limited in its scope to the details of construction and arrangement of components set forth in the following description or illustrated in the drawings. Other embodiments of the disclosure are capable of being practiced or carried out in various ways. Also, in describing the embodiments, specific terminology will be resorted to for the sake of clarity. It is intended that each term contemplates its broadest meaning as understood by those skilled in the art and includes all technical equivalents which operate in a similar manner to accomplish a similar purpose.

[0052] Herein, the use of terms such as “having,” “has,” “including,” or “includes” are open-ended and are intended to have the same meaning as terms such as “comprising” or “comprises” and not preclude the presence of other structure, material, or acts. Similarly, though the use of terms such as “can” or “may” are intended to be open-ended and to reflect that structure, material, or acts are not necessary, the failure to use such terms is not intended to reflect that structure, material, or acts are essential. To the extent that structure, material, or acts are presently considered to be essential, they are identified as such.

[0053] By “comprising” or “containing” or “including” is meant that at least the named compound, element, particle, or method step is present in the composition or article or method, but does not exclude the presence of other compounds, materials, particles, method steps, even if the other such compounds, material, particles, method steps have the same function as what is named.

[0054] It is also to be understood that the mention of one or more method steps does not preclude the presence of additional method steps or intervening method steps between those steps expressly identified.

[0055] The components described hereinafter as making up various elements of the disclosure are intended to be illustrative and not restrictive. Many suitable components that would perform the same or similar functions as the components described herein are intended to be embraced within the scope of the disclosure. Such other components not described herein can include, but are not limited to, for example, similar components that are developed after development of the presently disclosed subject matter.

[0056] Liquefied Natural Gas (LNG) regasification systems are currently an untapped source of cold energy. In these systems, LNG is vaporized at terminals into natural gas. These terminals operate at large scale in coastal regions, and the latent heat of vaporization is transferred to seawater and exhausted back into the ocean. Indeed, about 95% of the regasification processes are conducted by heat exchange with seawater, which wastes the exergy (i.e., the available energy capable of doing useful work) of LNG and also raises concerns for local ecosystems. The regasification process can be integrated by heat exchange with other processes instead, including the Rankine vapor cycle, air separation unit (ASU), adsorbed natural gas, and post-combustion CO_2 capture, to provide cold energy to those processes.

[0057] In the present disclosure, the cold energy from LNG regasification or external cooling cycles can enable cost-efficient DAC at near-cryogenic temperatures (160-240 K). DAC at near-cryogenic temperatures is expected to enable the use of adsorbents with low heats of adsorption for CO_2, which can reduce energy and capital costs via significant enhancements in working capacity. Part of the cold energy provided by LNG regasification or a cooling loop can be used to condense out water vapor in air during early stages of heat exchange, resulting in cold air with sub-ppm levels of water vapor. This low water concentration also enables the use of many physisorbents that have been ruled out for DAC.

[0058] The potential of physisorbents under near-cryogenic DAC conditions was initially evaluated through large-scale grand canonical Monte Carlo (GCMC) simulations of the CoRE-MOF database with density derived electrostatic and chemical (DDEC) charges. Notably, the structure-property relationships learned from the CoRE-MOF database are not confined to MOFs and can be extended to other classes of sorbents. Based on these simulations, CO_2 adsorption

equilibrium uptakes of four physisorbents–MIL-120(Al), Zeolite 5A, Zeolite 13X, and CALF-20–were examined under various near-cryogenic temperatures in volumetric adsorption apparatuses. Among these adsorbent candidates, Zeolite 13X and CALF-20 were selected and further examined by dynamic breakthrough analysis at 195 K. The experimental results were used to perform techno-economic analyses of near-cryogenic DAC processes incorporating thermal coupling with LNG regasification were performed. The potential scale of carbon capture via LNG-DAC deployment was also assessed to illustrate the long-term impact of the concept on global climate change scenarios. In addition, the compressor input work required for near-cryogenic DAC employing a refrigeration cycle was evaluated.

[0059] Reference will now be made in detail to exemplary embodiments of the disclosed technology, examples of which are illustrated in the accompanying drawings and disclosed herein. Wherever convenient, the same references numbers will be used throughout the drawings to refer to the same or like parts.

[0060] FIG. 1 is a schematic diagram of a direct air capture (DAC) system 100. The DAC system 100 comprises a sorbent bed 110, a heat exchanger 120, and a feed line 130. In the case of the DAC system 100, the feed line 130 is connected to the sorbent bed 110 and provides a first fluid to the sorbent bed 110 from the heat exchanger 120 such that the first fluid can contact a sorbent material in the sorbent bed 110. The heat exchanger 120 conducts a heat exchange between the first fluid and a second fluid in order to precool the first fluid prior to contacting the sorbent material in the sorbent bed 110. The sorbent bed 110 operates at a temperature from 160 K to 240 K (e.g., from 160 K to 230 K, from 160 K to 220 K, from 170 K to 230 K, from 180 K to 220 K, from 170 K to 220 K, from 190 K to 210 K, from 160 K to 210 K, or from 160 K to 200 K). As would be appreciated, the sorbent bed 110 can achieve such an operating temperature due to the first fluid being precooled prior to entering the sorbent bed 110 such that the fluid has a temperature from 160 K to 240 K (e.g., from 160 K to 230 K, from 160 K to 220 K, from 170 K to 230 K, from 180 K to 220 K, from 170 K to 220 K, from 190 K to 210 K, from 160 K to 210 K, or from 160 K to 200 K) upon entering the sorbent bed 110. However, it is understood that additional cooling mechanisms, either to cool the first fluid or the sorbent bed 110 itself, are contemplated.

[0061] In such a manner the first fluid can have a very low absolute humidity due at least in part to the precooling prior to entering the sorbent bed 110. The first fluid can have an absolute humidity from 0.4 ppb to 273 ppm once reaching the operating temperature of 160 K to 240 K.

The DAC system 100 can comprise additional unit operations to help the first fluid achieve this absolute humidity in addition to the heat exchanger 120, such as a desiccant bed. The heat exchanger 120, or some other unit operation in the DAC system 110, can also remove water from the first fluid which condenses as a result of the precooling and subsequent low temperature range. For example, the DAC system 100 can comprise a condenser, or the heat exchanger 120 can remove the condensed water.

[0062] The heat exchanger 120 can receive liquefied natural gas as the second fluid and conduct a heat exchange between the liquefied natural gas and the first fluid. This heat exchange can be conducted as part of a regasification process for the liquified natural gas. In such a manner, the cooling energy of the regasification process can be leveraged to precool the first fluid prior to the first fluid entering the sorbent bed.

[0063] FIG. 2 is a schematic diagram of a direct air capture (DAC) apparatus 200. The DAC apparatus comprises the sorbent bed 110 and the feed line 130. In the case of the DAC apparatus 200, the feed line 130 is connected to the sorbent bed 110 and provides a fluid to the sorbent bed 110 such that the fluid can contact a sorbent material in the sorbent bed 110. The sorbent bed 110 operates at a temperature from 160 K to 240 K (e.g., from 160 K to 230 K, from 160 K to 220 K, from 170 K to 230 K, from 180 K to 220 K, from 170 K to 220 K, from 190 K to 210 K, from 160 K to 210 K, or from 160 K to 200 K). As would be appreciated, the sorbent bed 110 can achieve such an operating temperature due to the fluid being precooled prior to entering the sorbent bed 110 such that the fluid has a temperature from 160 K to 240 K (e.g., from 160 K to 230 K, from 160 K to 220 K, from 170 K to 230 K, from 180 K to 220 K, from 170 K to 220 K, from 190 K to 210 K, from 160 K to 210 K, or from 160 K to 200 K) upon entering the sorbent bed 110. However, it is understood that additional cooling mechanisms, either to cool the fluid or the sorbent bed 110 itself, are contemplated.

[0064] In such a manner, the fluid, or the first fluid, can have a very low absolute humidity due at least in part to the precooling prior to entering the sorbent bed 110. The fluid, or the first fluid, can have an absolute humidity from 0.4 ppb to 273 ppm once reaching the operating temperature of 160 K to 240 K.

[0065] The fluid, or the first fluid, comprises CO_2. In such a manner, the sorbent material in the sorbent bed 110 is configured to adsorb CO_2 from the fluid, or the first fluid, when it is in contact with the sorbent material. Further, the CO_2 can be desorbed from the sorbent material, and a

desorption line connected to the sorbent bed 110 can remove the desorbed CO_2 from the sorbent bed 110.

[0066] The desorption of the CO_2 from the sorbent bed 110 can be conducted after the sorbent material is saturated. The desorption process can operate from 273 K to 303 K. As would be appreciated by those of skill in the art, the desorption process can operate at approximately room temperature. Further, the desorption process can operate from 0.05 bar to 0.3 bar (e.g., from 0.06 bar to 0.3 bar, from 0.07 bar to 0.3 bar, from 0.08 bar to 0.3 bar, from 0.09 bar to 0.3 bar, from 0.1 bar to 0.3 bar, from 0.05 bar to 0.2 bar, or from 0.05 bar to 0.1 bar), thereby providing for vacuum desorption.

[0067] Alternatively, or in addition, to the vacuum desorption described above, the desorption of the CO_2 from the sorbent bed 110 can be conducted using a purging gas. The purging gas can be, for example, high-purity CO_2. Further, the desorption process can operate from 273 K to 623 K (e.g., from 280 K to 620 K, from 290 K to 610 K, from 300 K to 600 K, from 400 K to 600 K, or from 500 K to 600 K). The desorption process can operate from 0.5 bar to 1.2 bar. As would be appreciated by those of skill in the art, the desorption process can operate at approximately atmospheric pressure.

[0068] As described above, the sorbent bed 110 comprises a sorbent material. The sorbent material is defined by material properties, including crystal density, largest cavity diameter, and total pore volume. The sorbent material has a crystal density from 0.2 g/cm^3 to 2 g/cm^3 (e.g., 0.3 g/cm^3 to 1.9 g/cm^3, from 0.4 g/cm^3 to 1.8 g/cm^3, from 0.5 g/cm^3 to 1.7 g/cm^3, or from 0.6 g/cm^3 to 1.6 g/cm^3), a largest cavity diameter from 4 Å to 16 Å (e.g., from 5 Å to 15 Å, from 6 Å to 14 Å, from 7 Å to 13 Å, or from 8 Å to 12 Å), and a total pore volume from 0.2 cm^3/g to 1.5 cm^3/g (e.g., from 0.3 cm^3/g to 1.4 cm^3/g, from 0.4 cm^3/g to 1.3 cm^3/g, from 0.5 cm^3/g to 1.2 cm^3/g, from 0.6 cm^3/g to 1.1 cm^3/g, or from 0.7 cm^3/g to 1 cm^3/g).

[0069] The sorbent material can have a heat of adsorption of 60 kJ/mol or less (e.g., from 36 kJ/mol to 60 kJ/mol, from 37 kJ/mol to 60 kJ/mol, from 38 kJ/mol to 60 kJ/mol, from 39 kJ/mol to 60 kJ/mol, from 40 kJ/mol to 60 kJ/mol, from 45 kJ/mol to 60 kJ/mol, from 50 kJ/mol to 60 kJ/mol, from 40 kJ/mol to 55 kJ/mol, from 40 kJ/mol to 50 kJ/mol, or from 36 kJ/mol to 50 kJ/mol).

[0070] The sorbent material can have a CO_2 / N_2 selectivity of 10^5 or greater (e.g., 2 x 10^5 or greater, 3 x 10^5 or greater, 4 x 10^5 or greater, or 5 x 10^5 or greater). As would be understood, the selectivity of the sorbent material is defined as adsorption selectivity, according to

$\alpha_{12}^{ads}=(N_1^{ads}/N_2^{ads})\ (y_2/y_1)$. In other words, the purity of CO_2, with the assumption that all adsorbed gases release during desorption, can be 80% or greater (e.g., 85% or greater, 90% or greater, 95% or greater, 98% or greater, 99% or greater, or 99.9% or greater).

[0071] The sorbent material can have a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater (e.g., from 3.4 to 8.0 mmol CO_2/g of sorbent material, from 3.5 to 8.0 mmol CO_2/g of sorbent material, from 3.6 to 8.0 mmol CO_2/g of sorbent material, from 3.7 to 8.0 mmol CO_2/g of sorbent material, from 3.9 to 8.0 mmol CO_2/g of sorbent material, from 4.0 to 8.0 mmol CO_2/g of sorbent material, from 3.4 to 7.0 mmol CO_2/g of sorbent material, or from 3.4 to 5.5 mmol CO_2/g of sorbent material) at 160 K. The sorbent material can have a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater (e.g., from 2.5 to 8.0 mmol CO_2/g of sorbent material, from 3.0 to 8.0 mmol CO_2/g of sorbent material, from 3.4 to 8.0 mmol CO_2/g of sorbent material, from 3.5 to 8.0 mmol CO_2/g of sorbent material, from 3.6 to 8.0 mmol CO_2/g of sorbent material, from 3.7 to 8.0 mmol CO_2/g of sorbent material, from 3.9 to 8.0 mmol CO_2/g of sorbent material, from 4.0 to 8.0 mmol CO_2/g of sorbent material, from 3.4 to 7.0 mmol CO_2/g of sorbent material, from 3.4 to 5.5 mmol CO_2/g of sorbent material, from 2.0 to 7.0 mmol CO_2/g of sorbent material, or from 2.0 to 5.5 mmol CO_2/g of sorbent material) at 180 K. The sorbent capacity can be tested under 400 ppm CO_2/N_2.

[0072] FIG. 3 is a flowchart illustrating a direct air capture (DAC) process 300. As shown, the DAC process 300 comprises conducting 302 a heat exchange between a fluid and liquefied natural gas. For example, the heat exchange can be conducted in the heat exchanger 120. The liquefied natural gas has a temperature from 100 K to 190 K (e.g., from 110 K to 180 K, from 120 K to 170 K, from 130 K to 160 K, or from 140 K to 150 K), and the fluid can be cooled to a temperature from 160 K to 240 K (e.g., from 160 K to 230 K, from 160 K to 220 K, from 170 K to 230 K, from 180 K to 220 K, from 170 K to 220 K, from 190 K to 210 K, from 160 K to 210 K, or from 160 K to 200 K).

[0073] The DAC process 300 further comprises contacting 304 the fluid with a sorbent material as described above. The fluid comprises CO_2, and the sorbent material can be configured to adsorb CO_2. The material properties of the sorbent material are described in greater detail above.

[0074] The DAC process 300 further comprises adsorbing 306 the CO_2 from the fluid into the sorbent material. The adsorbing 306 can continue until the sorbent material is saturated, at which

point the DAC process can further comprise desorbing the CO_2 from the sorbent material, as described in greater detail above.

[0075] Certain embodiments and implementations of the disclosed technology are described above with reference to block and flow diagrams of systems and methods according to example embodiments or implementations of the disclosed technology. It will be understood that one or more blocks of the block diagrams and flow diagrams, and combinations of blocks in the block diagrams and flow diagrams, respectively, can be implemented by computer-executable program instructions. Likewise, some blocks of the block diagrams and flow diagrams may not necessarily need to be performed in the order presented, may be repeated, or may not necessarily need to be performed at all, according to some embodiments or implementations of the disclosed technology.

[0076] It is to be understood that the embodiments and claims disclosed herein are not limited in their application to the details of construction and arrangement of the components set forth in the description and illustrated in the drawings. Rather, the description and the drawings provide examples of the embodiments envisioned. The embodiments and claims disclosed herein are further capable of other embodiments and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein are for the purposes of description and should not be regarded as limiting the claims.

[0077] Accordingly, those skilled in the art will appreciate that the conception upon which the application and claims are based may be readily utilized as a basis for the design of other structures, methods, and systems for carrying out the several purposes of the embodiments and claims presented in this application. It is important, therefore, that the claims be regarded as including such equivalent constructions.

[0078] Furthermore, the purpose of the foregoing Abstract is to enable the United States Patent and Trademark Office and the public generally, and especially including the practitioners in the art who are not familiar with patent and legal terms or phraseology, to determine quickly from a cursory inspection the nature and essence of the technical disclosure of the application. The Abstract is neither intended to define the claims of the application, nor is it intended to be limiting to the scope of the claims in any way. Instead, it is intended that the invention is defined by the claims appended hereto.

Examples

[0079] The following sections illustrate example implementations of the present disclosure/disclosed technology:

[0080] In LNG regasification, the vaporization temperature of LNG can vary between 109 K and 190 K depending on the storage pressure of LNG. After vaporization, the natural gas is heated to around room temperature (up to 283 K) before being supplied into pipeline networks. Therefore, the thermal coupling of DAC with LNG regasification can enable adsorption temperatures between 109 K and 283 K. In this example of the present disclosure, a suitable range of adsorption temperature for the near-cryogenic DAC process is between 160 and 240 K (FIG. 5A). Without wishing to be bound by any particular scientific theory, at temperatures lower than 160 K, it is likely that competitive adsorption of O_2 and N_2 will become an issue for CO_2 product purity and recovery. At temperatures higher than 220 K, there are simply too few physisorbents that can successfully capture CO_2 from air with a high working capacity. An important feature of the present disclosure is that the disclosed cooling of the air to 160–240 K removes nearly all water that is present at ambient air via condensation. For example, 50% relative humidity at 283 K corresponds to 6,100 ppm of water, but the same relative humidity at 160 K yields a water concentration of only $3.95 \cdot 10^{-4}$ ppm.

[0081] In the disclosed DAC processes and systems coupled with LNG regasification, the feed air flow is first cooled down to the adsorption temperature of the adsorbent materials (160 K–240 K). The cooling can be achieved by heat exchange in the LNG evaporator, and during the process the water vapor in the air almost completely freezes out. Alternatively, the water vapor could condense and be removed before freezing during the initial few heat exchanger stages. Then, the cold, dry air passes through the adsorbent bed, simultaneously cooling the bed and providing CO_2 for capture (FIG. 5A). In this process, the cold energy from the LNG regasification process is used to compensate for four enthalpy changes: (1) cooling the feed air, (2) cooling and condensing or freezing water, (3) cooling the adsorbent bed, and (4) mitigating heating of the adsorption bed due to CO_2 adsorption.

[0082] After the adsorption process, the bed is isolated from gas flow and heated up to around room temperature (~283 K) by heat exchanging with seawater. If this temperature is insufficient for recovery of the given sorbent, it can be further increased to a higher desorption temperature (e.g., 473 K) by external thermal energy (e.g., heat from natural gas combustion). Various desorption processes can be considered depending on the characteristics of the sorbent used.

Notably, the near-cryogenic DAC has the potential to utilize physisorbents, which are suitable for desorption with high-purity CO_2 as a desorbent gas at elevated temperature (> 423 K), at which amine sorbents may become unstable. Using high-purity CO_2 to sweep desorbed CO_2 out of the bed can achieve high CO_2 product purity and obviate the need of vacuum systems (FIG. 4B). Alternatively, vacuum-assisted desorption at relatively lower temperatures could also be considered to reduce thermal energy costs (FIG. 4C). It is worth noting that the cycle can also produce fresh water and pre-cooled air for an ASU, which could generate additional profit.

[0083] As mentioned, the adsorption at near-cryogenic temperatures can enable the use of physisorbents with low heats of adsorption. These physisorbents have insufficient interaction with CO_2 for room-temperature DAC and typically have very low CO_2 uptake from the ambient air (FIG. 5A). However, as would be understood by those of ordinary skill in the art, exothermic physisorption is thermodynamically much more favored at near-cryogenic temperatures and can result in high working capacity (FIG. 5B).

[0084] Exact prediction of the CO_2 adsorption behavior of individual MOFs at extremely dilute conditions (0.0004 bar) by molecular simulations with a generic force field is very challenging; however, their trends are still instructive. Large-scale molecular simulations can be conducted for crystallographic structures in the CoRE-MOF-DDEC database to explore the potential of CO_2 physisorption for near-cryogenic DAC. Lowering the adsorption temperature strongly increases CO_2 adsorption at low loadings (FIG. 6). As would be appreciated by those of ordinary skill in the art, the Henry's constant for CO_2 adsorption increases exponentially when the temperature is reduced from 298 K to 240 and 160 K while the heat of adsorption ($\Delta\widehat{H}_s$) was largely unchanged over that same temperature range. Henry's constants of promising DAC materials at room temperature can be calculated to identify potential materials for near-cryogenic DAC. A heat of sorption ($\Delta\widehat{H}_s$) of -60 kJ/mol has been suggested as a benchmark for DAC sorbents operating at ambient conditions. Henry's constant can be calculated at 298 K for all of the MOFs with heats of sorption around -60 kJ/mol, finding an average Henry's constant of 0.139 mol kg^{-1} Pa^{-1}. At lower temperatures, calculations on the CoRE-MOF database materials show that this Henry's constant can be achieved with materials with much lower sorption enthalpies (i.e., between -40 and -24 kJ/mol for 220 and 160 K, respectively). This finding identified a large number of candidate adsorbents for DAC at near-cryogenic conditions (FIG. 6).

[0085] Lowering the DAC adsorption temperature narrows the gap between the optimal physical properties of DAC adsorbents and the typical properties of physisorbents (FIG. 7). At room temperature, the properties of MOFs suitable for DAC diverge from those of most MOFs in the CoRE-MOF database. For example, most of the adsorbents suitable for DAC at 298 K have their crystal density between 1.50 $g \cdot cm^{-3}$ (1^{st} quartile) and 1.92 $g \cdot cm^{-3}$ (3^{rd} quartile), which shows minimal overlap with the crystal density distribution of all structures in CoRE-MOF-DDEC, where the 1^{st} and 3^{rd} quartiles are 1.03 $g \cdot cm^{-3}$ and 1.51 $g \cdot cm^{-3}$, respectively. However, at lower adsorption temperatures, a substantially larger fraction of the CoRE-MOF-DDEC structures—including some well-known MOFs—falls within the optimal crystal density range for DAC (Table I).

Table I. 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.

Condition the optimal structures were selected under	Crystal density ($g \cdot cm^{-3}$)		Pore volume ($cc \cdot g^{-1}$)		Largest cavity diameter (Å)		Pore limiting diameter (Å)		Gravimetric surface area ($m^2 \cdot g^{-1}$)		Volumetric surface area ($m^2 \cdot cm^{-3}$)		Helium void fraction	
	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	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

[0086] Similar to the crystal density, the largest cavity diameter (LCD), total pore volume (V_p) (FIG. 7), and other physical properties (gravimetric surface area, volumetric surface area, PLD, helium void fraction) of adsorbents for DAC application shift closer to those of most CoRE MOFs when the adsorption temperature is reduced to 240 or 160 K. Without wishing to be bound by any particular scientific theory, these data show that it will likely be easier to develop practical materials for near-cryogenic DAC than for DAC at ambient conditions. In addition, shifting to a larger LCD and V_p implies that a higher probability of large CO_2 uptake, since adsorbents with higher LCD and V_p generally have higher saturation uptake for CO_2. In particular, the new peaks formed in the LCD range of 9.7 Å to 16.1 Å and in the V_p range of 0.73 $cc \cdot g^{-1}$ to 1.55 $cc \cdot g^{-1}$ under

near-cryogenic DAC conditions highlight opportunities for very high CO_2 uptake compared with amine sorbents. The LCD regions are also where some common adsorbents are located, namely, Zeolite 13X, MIL-53(Al), HKUST-1, MOF-74(Co), and others.

[0087] The opportunity for high CO_2 uptake in near-cryogenic DAC can be explored by GCMC simulations. At 298 K, no adsorbent in the database could surpass 3 mmol/g of CO_2 uptake unless its sorption enthalpy was more exothermic than -60 kJ/mol. In contrast, many structures, especially those with sorption enthalpies between -36 and -60 kJ/mol, exhibited CO_2 uptakes exceeding 4 mmol/g at 220 K. Based on these molecular simulations, a guideline for identifying promising materials for near-cryogenic DAC can be established (Table II). Two examples using this guideline are Zeolite 13X and CALF-20, while MIL-120(Al) and Zeolite 5A also showed potential, though to a lesser extent. These four examples are evaluated further herein.

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

Candidates	Crystal density ($g \cdot cm^{-3}$)		Pore volume ($cc \cdot g^{-1}$)			Largest cavity diameter (Å)			Pore limiting diameter (Å)		Gravimetric surface area ($m^2 \cdot g^{-1}$)		Volumetric surface area ($m^2 \cdot cm^{-3}$)		Helium void fraction	
	1st quartile	3rd quartile	1st	3rd	Extra*	1st	3rd	Extra*	1st	3rd	1st	3rd	1st	3rd	1st	3rd
	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		*614*		*963*		0.432	
Zeolite 5A	*1.42***		0.298			9.53			*3.86*		*677*		*962*		0.424	
Zeolite 13X	*1.41*		*0.322*			*10.4*			5.89		*871*		*1230*		*0.503*	
CALF-20	*1.38*		*0.403*			*5.06*			4.39		*583*		803		*0.560*	

* Physical property region suggested for high CO_2 uptake/working capacity under near-cryogenic DAC condition.
** Physical property that satisfies the criteria appears in italics and bold text.

[0088] The examples herein also can use experimental measurements to address the competitive adsorption of CO_2 and N_2 as well. Single-component adsorption experiments can be carried out with each gas, and ideal adsorbed solution theory (IAST) can be used to predict mixture adsorption. The first example, MIL-120(Al), has a desirable isostructure with MIL-120(Ga), which showed good uptake at 220 K to 240 K in GCMC simulations (Table III). However, experimental results revealed that MIL-120(Al) may have better performance below 220 K to achieve sufficient CO_2

uptakes at 40 Pa (2.02 mmol/g at 180 K and 3.46 mmol/g at 160 K, FIG. 8A). At these low temperatures, N_2 adsorption is also enhanced significantly compared to higher temperatures. IAST calculations based on experimental single-component data predict that N_2 is non-negligibly concentrated in the adsorbed phase on MIL-120(Al) at 160 K (FIG. 8B). The CO_2/N_2 selectivity at these conditions is predicted to be 654, which is insufficient for DAC CO_2 purity targets. This example highlights the need to find materials exhibiting both high capacity for CO_2 and very high selectivity for CO_2 over N_2 under near-cryogenic conditions.

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

	$\Delta\widehat{H}_s$ (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)	$q_{CO2,220\ K}$ (mmol/g)
MIL-120(Ga)	-52.0	$2.99\cdot10^6$	0.167	$1.79\cdot10^7$	62.7	3.53

[0089] Zeolite 5A and Zeolite 13X are two additional examples for near-cryogenic DAC not only because their physical properties align well with the guidance established above (Table II), but also because they are known to have strong interactions with CO_2. Their CO_2 adsorption isotherms at 180–220 K revealed that both zeolites have significant CO_2 uptake at 40 Pa (FIG. 8A and FIG. 9). However, Zeolite 5A exhibits limited CO_2/N_2 selectivity similar to MIL-120(Al), probably due to its small pore sizes which are favorable for N_2 (FIG. 8B). In contrast, Zeolite 13X exhibited much higher CO_2/N_2 selectivity (~10^6) than MIL-120(Al) and Zeolite 5A.

[0090] Zeolite 13X has significantly larger pore sizes (~10 Å) and pore volumes (0.27 $cc\cdot g^{-1}$) than Zeolite 5A, which can provide large saturation CO_2 loadings (~8.5 mmol/g). At 40 Pa and 200 K, Zeolite 13X utilizes almost half of its large pore volume for CO_2 adsorption (4.1 mmol/g). Notably, the DAC performance of Zeolite 13X observed in this example (4.1–5.5 mmol/g at 195–200 K) is nearly double the performance at extremely cold sub-ambient temperatures (~2.8 mmol/g at 215 K), further emphasizing the advantages of near-cryogenic DAC. CO_2 equilibrium uptake of Zeolite 13X at 473 K and 1 bar is 0.56 mmol/g (FIG. 10A), which indicates high CO_2 working capacity under desorption using high-purity CO_2 sweep gas.

[0091] CALF-20 is a MOF of considerable interest due to its promising CO_2 adsorption behavior, scalable synthesis, and long-term stability even under steam desorption conditions, also demonstrated significant CO_2 sorption capacity at 195 K (~4.3 mmol/g, FIG. 9 and FIG. 10B).

This observation is particularly remarkable, considering that CALF-20 had previously shown negligible CO_2 sorption (<0.1 mmol/g) from DAC-level dilute CO_2 sources. IAST results indicated that CALF-20 adsorbs CO_2 almost exclusively over N_2 at 195 K, with a CO_2/N_2 adsorption selectivity exceeding $4 \cdot 10^5$, well beyond the requirements for DAC purity targets. At near room temperature (283–303 K), CALF-20 exhibits low CO_2 uptakes, consistent with previous observations of its desorbability under mild conditions. These characteristics suggest potential use of CALF-20 for vacuum-assisted desorption under near-room temperatures (FIG. 10B). Given their extraordinary performance under near-cryogenic DAC conditions, scalability, and long-term stability, the examples of Zeolite 13X and CALF-20 can be analyzed for further mixture adsorption testing using dynamic breakthrough analysis.

[0092] Dynamic breakthrough analysis on Zeolite 13X and CALF-20 powder columns can be performed at 195 K using a dry ice/ethanol cooling bath. The Zeolite 13X powder-packed bed exhibited highly favorable DAC performance: approximately 5.5 mmol/g of CO_2 pseudo-equilibrium capacity from 100 sccm of simulated air (400 ppm CO_2 in N_2 balance) (FIG. 11A). The capacity aligns well with single-component CO_2 uptake of Zeolite 13X at 40 Pa and 195 K (FIG. 10A), consistent with exceptionally high CO_2/N_2 selectivity from IAST. The high pseudo-equilibrium capacity is also observed at the higher flow rate of 200 sccm (FIG. 11A), indicating that the system is not strongly limited by adsorption kinetics even at low temperatures within this flow regime. However, when the CO_2 breakthrough curves with an N_2 balance were compared to those with a He balance, the curves are less sharp and have larger mass transport zones (FIGs. 11A and 11B). This effect is more pronounced at the 200 sccm flow rate, where the adsorption speed under a He balance was much faster than under an N_2 balance, implying slower adsorption kinetics in the N_2 atmospheres, as expected given the relative magnitudes of CO_2–He and CO_2–N_2 gas-gas diffusivities. Overall, the results indicate the presence of some competitive adsorption kinetic limitations at 195 K. The adsorbed CO_2 can be recovered almost fully by heating the bed up to 200 °C while flowing He (FIG. 11C). The purity of the desorbed gas is high (94%) despite the probable presence of some N_2 in the interstitial volume of the column after the initial He sweep.

[0093] CALF-20 can also exhibit an extraordinary pseudo-equilibrium capacity of 4.5 mmol/g from 100 sccm of simulated air (400 ppm CO_2 in N_2 balance) at 195 K (FIG. 12A and FIG. 12B). Considering the sample amount in the fixed bed and CO_2 uptakes, the overall sorption kinetics of Zeolite 13X and CALF-20 are comparable under a flow rate of 100 sccm. After the first adsorption

cycle, the column can be exposed to a vacuum of approximately 0.08 bar while being heated to 22 °C (FIG. 12C). Desorbed CO_2 under the near–room–temperature desorption can be quantified as 3.9 mmol/g, highlighting the feasibility of CALF-20 desorption at low temperatures. A second adsorption cycle can be conducted under 200 sccm of simulated air (in N_2 balance), which results in a pseudo-equilibrium capacity of 3.4 mmol/g, which is around 76% of the adsorbed CO_2 during the initial adsorption (FIG. 12B).

[0094] Based on the experimental results, the thermal and electric energy requirements for the near-cryogenic DAC using Zeolite 13X and CALF-20 can be estimated and compared with those of ambient DAC using an amine sorbent. Unlike the ambient DAC process, which requires only fan energy (E_{fan}) during adsorption, the near-cryogenic DAC process demands significant amounts of cold energy, mainly for cooling down (C_{air}=247.6 GJ/tCO_2) and dehumidifying (C_{humid}=41.8 GJ/tCO_2) atmospheric air at the global average temperature (14–15 °C). Providing cold energy at such a scale through an external cooling cycle is economically prohibitive, making coupling with LNG regasification desirable unless the process is conducted in naturally cold climates. In the LNG-DAC process, the cold energy from LNG regasification (290.4 GJ/tCO_2) can compensate for all four thermal energy requirements during the adsorption process, namely, C_{air}, C_{humid}, C_{ads} (energy for cooling adsorbents), and C_{hoa} (heats of adsorption). To meet these significant cold energy demands, 327.9 tons of LNG can be regasified per ton of CO_2 captured. With advancements in adsorbent materials and process design, LNG consumption could decrease to 30.1 tLNG/tCO_2. Aside from the cold energy, adsorption under near-cryogenic conditions incurs a slightly higher E_{fan} owing to less efficient mass transport at the temperatures.

[0095] Near-cryogenic DAC can demonstrate significant energy savings in the desorption process compared to ambient DAC. The energy requirements of ambient DAC using amine sorbents can be estimated assuming an annual sorbent degradation rate of 50% and 70–90% recovery of water latent heat. The results indicate that the conventional temperature-vacuum adsorption (TVSA) process with amine sorbents requires substantial thermal energy (12.9–17.8 GJ/tCO_2) and electrical energy (5.5 GJ/tCO_2). The energy associated with water desorption ($Q_{sen,H2O}$, $Q_{lat,H2O}$, and $E_{vac,H2O}$) is a significant contributor, accounting for 42–54% of the total energy consumption. When sorbent degradation is assumed to be negligible, the thermal energy requirements were 9.1–14 GJ/tCO_2, which is comparable to previous studies.

[0096] In contrast, the LNG-DAC process eliminates the water-related energy costs. Additionally, when using a material such as Zeolite 13X, employing a high-purity CO_2 as a sweep gas further reduces desorption energy consumption by eliminating the need for vacuum pump operation. After accounting for the energies compensated by heat exchange with seawater during bed heating step, the thermal energy input required for desorption is 2.0 GJ/tCO_2. These low thermal energy requirements are also attributed to the advantages of physisorbents in working capacity, heat of adsorption, and specific heat capacity of sorbents. Considering CO_2 emissions from the production of thermal energy for process operations, the overall energy requirement for adsorption and desorption of the Zeolite 13X system amounts to 3.3 GJ/t$CO_{2,net}$.

[0097] On the other hand, the near-cryogenic DAC with CALF-20 is designed to perform desorption at ambient temperature (283 K), which can be achieved through heat exchange with seawater or other low-grade heat sources. As a result, the CALF-20 system requires no additional thermal energy input for desorption and relies exclusively on electrical energy for vacuum pump and fan operation. In terms of energy efficiency, the CALF-20 system outperformed the Zeolite 13X system, with a total energy requirement of 1.7 GJ/t$CO_{2,net}$.

[0098] Finally, the levelized cost of capture (LCOC) for near-cryogenic DAC can be evaluated compared to ambient DAC. For a conventional ambient DAC using amine sorbents, the primary contributors to the LCOC (171.3 USD/tCO_2) are the energy costs associated with managing water co-adsorbed with CO_2 (35% of LCOC) and the costs related to the sorbent contactor, including $OPEX_{ads}$ (5.6%), $CAPEX_{cont,ann}$ (19.3%), and $Q_{sen,ads}$ (12.8%). The water-related components of the LCOC are primarily influenced by sorbent material parameters such as the ratio of CO_2 working capacity to water working capacity (r_{H_2O/CO_2}), the heat of water adsorption ($\Delta\widehat{H}_{s,amine,H_2O}$), and the recovery efficiency of water latent heat ($\eta_{lat,rec}$). Other main contributors, $OPEX_{ads}$, $CAPEX_{cont,ann}$, and $Q_{sen,ads}$ are largely dependent on factors such as annual sorbent degradation (r_{deg}), contactor cost (C_{cont}), and CO_2 working capacity (wc).

[0099] The near-cryogenic DAC process of the present examples provides significant improvements in all the main cost-driving parameters identified in conventional DAC. The Zeolite 13X system achieves massive cost reductions by eliminating water desorption-related expenses and vacuum energy costs. In addition, it shows notable improvement in $OPEX_{ads}$, $CAPEX_{cont,ann}$, and $Q_{sen,ads}$ from amine sorbent-based system due to enhanced sorbent characteristics, including wc (1.7 mmol/g → 5 mmol/g) and r_{deg} (0.5 → 0). Overall, the LNG-DAC process with Zeolite

13X is projected to reduce the LCOC by approximately 60%, achieving low-cost DAC at 68.2 USD/tCO_2.

[0100] The LNG-DAC process with CALF-20 also demonstrates a promising LCOC (86.3 USD/tCO_2) by eliminating water desorption-related costs and thermal energy costs. The main contributor to the higher LCOC compared to the Zeolite 13X system is the significantly higher $CAPEX_{ads,ann}$, resulting from the higher sorbent cost (C_{ads}, 20 USD/kg) of CALF-20 and its lower *wc* (1.8 mmol/g) due to low desorption temperature. That said, the relative economic feasibility of the Zeolite 13X and CALF-20 systems may vary depending on the prices of thermal and electrical energy (C_{elec} and C_{thrm}) and their efficiencies (η_{grid} and η_{thrm}).

[0101] Given the relatively uncommon adsorption conditions of near-cryogenic DAC, there is substantial potential to develop advanced sorbents that achieve high capture efficiency (~0.9) at relatively high temperatures (~240 K), thereby reducing the LNG/CO_2 ratio.

[0102] DAC at near-cryogenic temperatures can unlock the full potential of large-pore-volume physisorbents, offering exceptionally high CO_2 working capacity with lower desorption enthalpy. For example, Zeolite 13X exhibits nearly double the sorption capacity under DAC conditions at 195 K compared to the coldest sub-ambient DAC system in polar regions (215 K), underscoring the advantages of operating at lower temperatures. The energy required for near-cryogenic DAC, considering thermal coupling with LNG regasification, can be as low as 2.1–3.3 GJ/$tCO_{2,net}$. As a result, the levelized cost of capture (LCOC) for near-cryogenic DAC is estimated to be approximately half that of state-of-the-art amine sorbent-based systems. Near-cryogenic DAC also offers considerable potential for further energy efficiency improvements through integration with green processes such as Rankine cycles, air separation units (ASU), and hydrogen or ammonia production.

[0103] Molecular simulations in these examples demonstrate that near-cryogenic DAC offers an opportunity to employ a broad range of physisorbents. Zeolite 13X stands out as one example with a high CO_2 capacity of 5.5 mmol/g at 195 K. Similarly, CALF-20, despite underperforming in ambient or sub-ambient DAC conditions, achieves a notable CO_2 capacity of 4.5 mmol/g at 195 K. Beyond their high CO_2 capacities, both sorbents exhibit desirable characteristics such as low desorption enthalpy, cost efficiency, scalability, and long-term stability, all of which are essential for real-world applications. Under near-cryogenic conditions, the pool of potential DAC sorbents could expand to more than five times the number available at ambient conditions, providing further

opportunities to identify materials with superior attributes. Based on simulation results, sorbents with $\Delta\widehat{H}_s$ between -36 kJ/mol and -60 kJ/mol can be desirable for DAC at near-cryogenic temperatures.

CLAIMS

What is claimed is:

1. A direct air capture (DAC) apparatus comprising:

a sorbent bed comprising a sorbent material, the sorbent bed operating at a temperature from 160 K to 240 K, the sorbent material defined by:

a crystal density from 0.2 to 2 g/cm^3,

a largest cavity diameter from 4 to 16 Å, and

a total pore volume from 0.2 to 1.5 cm^3/g; and

a feed line connected to the sorbent bed, the feed line configured to provide a fluid to contact the sorbent material, the fluid comprising CO_2,

wherein the sorbent material is configured to adsorb the CO_2 from the fluid when the fluid is in contact with the sorbent material.

2. The DAC apparatus of Claim 1, wherein the sorbent material has a heat of adsorption of 60 kJ/mol or less.

3. The DAC apparatus of Claim 1, wherein the sorbent material has a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

4. The DAC apparatus of Claim 1, wherein the sorbent material has a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

5. The DAC apparatus of Claim 1, wherein the sorbent material has a CO_2 / N_2 selectivity of 4 x 10^5 or greater measured at a temperature from 160 K to 240 K.

6. The DAC apparatus of Claim 1, wherein the fluid in the feed line is precooled prior to contacting the sorbent material to reach the operating temperature from 160 K to 240 K.

7. The DAC apparatus of Claim 6, further comprising a heat exchanger connected to the feed line, the heat exchanger configured to receive liquefied natural gas and conduct a heat exchange

between the liquefied natural gas and the fluid in the feed line to precool the fluid in the feed line prior to contacting the sorbent material.

8. The DAC apparatus of Claim 7, wherein the liquefied natural gas exchanges heat with the fluid through the heat exchanger while undergoing a regasification process.

9. The DAC apparatus of Claim 1, further comprising a desorption line connected to the sorbent bed, the desorption line configured to remove CO_2 from the sorbent bed that has been desorbed from the sorbent material.

10. The DAC apparatus of Claim 9, wherein the sorbent bed is configured to undergo a desorption process operating at from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material to the desorption line.

11. The DAC apparatus of Claim 9, wherein the sorbent bed is configured to undergo a desorption process operating at from 393 K to 623 K and from 0.5 bar to 1.2 bar to release the CO_2 from the sorbent material to the desorption line, and the desorption process comprises contacting the sorbent bed with a purging gas.

12. A direct air capture (DAC) system comprising:

a sorbent bed comprising a sorbent material, the sorbent bed operating at a temperature from 160 K to 240 K, the sorbent material defined by:

a crystal density from 0.2 to 2 g/cm^3,

a largest cavity diameter from 4 to 16 Å, and

a total pore volume from 0.2 to 1.5 cm^3/g;

a heat exchanger configured to receive a second fluid and conduct a heat exchange between the second fluid and a first fluid in order to precool the first fluid prior to contacting the sorbent material; and

a feed line connecting the heat exchanger and the sorbent bed and configured to transport the first fluid from the heat exchanger to the sorbent bed,

wherein the first fluid comprises CO_2, and the sorbent material is configured to adsorb the CO_2 from the first fluid when the first fluid is in contact with the sorbent material.

13. The DAC system of Claim 12, wherein in the sorbent material has a heat of adsorption of 60 kJ/mol or less.

14. The DAC system of Claim 12, wherein the sorbent material has a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

15. The DAC system of Claim 12, wherein the sorbent material has a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

16. The DAC system of Claim 12, wherein the sorbent material has a CO_2 / N_2 selectivity of 4 x 10^5 or greater measured at a temperature from 160 K to 240 K.

17. The DAC system of Claim 12, wherein the second fluid is liquified natural gas.

18. The DAC system of Claim 17, wherein the liquefied natural gas exchanges heat with the fluid through the heat exchanger while undergoing a regasification process.

19. The DAC system of Claim 12, further comprising a desorption line connected to the sorbent bed, the desorption line configured to remove CO_2 from the sorbent bed that has been desorbed from the sorbent material.

20. The DAC system of Claim 19, wherein the sorbent bed is configured to undergo a desorption process operating at from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material to the desorption line.

21. A direct air capture (DAC) process comprising:

conducting a heat exchange between a fluid and liquefied natural gas, the liquefied natural gas having a temperature between 100 K and 190 K;

contacting the fluid with a sorbent material, the fluid being at a temperature from 160 K to 240 K, the fluid comprising CO_2 and the sorbent material defined by:

a crystal density from 0.2 to 2 g/cm^3,

a largest cavity diameter from 4 to 16 Å, and

a total pore volume from 0.2 to 1.5 cm^3/g; and

adsorbing the CO_2 from the fluid into the sorbent material.

22. The DAC process of Claim 21, wherein the sorbent material has a heat of adsorption of 60 kJ/mol or less.

23. The DAC process of Claim 21, wherein the sorbent material has a sorbent capacity of 3.4 mmol CO_2/g of sorbent material or greater as measured at 160 K.

24. The DAC process of Claim 21, wherein the sorbent material has a sorbent capacity of 2.0 mmol CO_2/g of sorbent material or greater as measured at 180 K.

25. The DAC process of Claim 21, wherein the sorbent material has a CO_2 / N_2 selectivity of 4 x 10^5 or greater measured at a temperature from 160 K to 240 K.

26. The DAC process of Claim 21, further comprising desorbing the CO_2 from the sorbent material, wherein the desorbing occurs from 273 K to 303 K and from 0.05 bar to 0.3 bar to release the CO_2 from the sorbent material.

27. The DAC process of Claim 21, further comprising desorbing the CO_2 from the sorbent material, wherein the desorbing occurs from 393 K to 623 K and from 0.5 bar to 1.2 bar to release the CO_2 from the sorbent material.

28. The DAC process of Claim 21, wherein the desorbing further comprises contacting the sorbent bed with a purging gas, and wherein the purging gas comprises high-purity CO_2.