

Toward A Greener Moisture Swing Technology for Distributed, Modular Direct Air Capture

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Summary

Several different types of moisture swing sorbents were found in the process of compiling information on how the technology works. This document examines the literature for approaches to moisture swing that might be conducive to an open hardware/open laboratory setting. Part 1 describes the moisture swing approach with ion exchange resin. Part 2 describes working with amines and the associated synthesis problems. Part 3 provides a look at better approaches, and suggests a method for moisture swing that appears promising to explore.

Introduction

A moisture swing approach to CO₂ removal was developed by Prof. Tao Wang in conjunction with Dr. Klaus Lackner and Dr. Allen Wright.¹ In that paper, the researchers present a means of absorbing CO₂ with a sorbent while it is dry, and releasing the CO₂ when the sorbent is wet. This absorption-desorption cycle under changing moisture conditions is why this has been described as a moisture swing technology. The sorbent is amine-containing and is mounted on flat sheets.

Amines are compounds that contain a specific nitrogen-containing chemical group, called an amine group. The specific amines that were used were in the form of quaternary ammonium cations attached to the polypropylene polymer structure making up each sheet.

While the above research uses carbonate ions to carry out the CO₂ removal, it is also possible to use phosphate ions to do the same. A paper in 2019 by Song *et al.*² demonstrated that this approach had a superior CO₂ absorption capacity and kinetics compared to the carbonate-based approach.

That paper also described several kinds of moisture swing sorbents. These were: porous polymers³ (functionalized through quaternization with ion exchange), modified carbon black⁴ (grafting of quaternized polymers to the high surface area material), ion-exchange resin (also quaternized), quaternized bamboo cellulose⁵ (research that was also done in Prof. Wang's lab), and quaternized chitosan aerogel.

All five of these different types of moisture swing sorbents notably have in common the process of quaternization with ion exchange. This feature unites all of the above sorbents and is what enables CO₂ removal by moisture swing.

¹ [Moisture Swing Sorbent for Carbon Dioxide Capture from Ambient Air | Environmental Science & Technology](#)

² [Moisture Swing Ion-Exchange Resin-PO4 Sorbent for Reversible CO2 Capture from Ambient Air | Energy & Fuels](#)

³ [Porous polymers prepared via high internal phase emulsion polymerization for reversible CO2 capture - ScienceDirect](#)

⁴ [Carbon black functionalized with hyperbranched polymers: synthesis, characterization, and application in reversible CO2 capture - Journal of Materials Chemistry A \(RSC Publishing\)](#)

⁵ [Preparation of Quaternized Bamboo Cellulose and Its Implication in Direct Air Capture of CO2 | Energy & Fuels](#)

Part 1. Moisture Swing by Ion Exchange Resin

Beyond the paper by Wang *et al.*, details of that moisture swing technology were made in a patent application by Wright and Lackner.⁶ The sorbent was an amine-based anion exchange resin formed into flat sheets; specifically the sorbent was described as the Anion I-200, available from Snowpure LLC, of San Clemente, California. It is a strong base Type 1 functionality ion exchange material that is supplied in Cl⁻ form.⁷ It is believed to be manufactured according to US patent 6,503,957.⁸

Physical and Chemical Characteristics: Further description of this material was available from a different paper⁹ which referenced this same material as Excellion membrane I-200, which is made from Excellion active resin extruded into a polypropylene membrane. Excellion is a product name from the same company, Snowpure. The Excellion active resin is described as a crosslinked chloromethylated polystyrene resin powder, quaternized with trimethylamine, and with its chloride ions exchanged for hydroxide ions such that the resin has quaternary ammonium hydroxide groups.

Performance Characteristics: The I-200 showed slow desorption/absorption profiles with a rate of $2.1 \times 10^{-3} \text{ mmol g}^{-1} \text{ min}^{-1}$ and a moderate swing size of $1.3 \times 10^{-1} \text{ mmol g}^{-1}$. It took over 2 hours to capture and release 130 $\mu\text{mol CO}_2$ per g of material. To accomplish this, the energy consumption is unknown but no heating of the water was needed. In fact, refrigeration was needed to control the humidity within the system; temperatures of -2 and 15 C were used to reach absolute humidities of 5 and 20 ppt which correspond to 20 and 95% relative humidity. Drying of the I-200 was accomplished through valves that let outside dry CO₂-containing air enter. A detailed description of the I-200's performance, including graphs, is available from the supplementary information here.¹⁰

The active material without being incorporated into the membrane had a rate of $3.5 \times 10^{-3} \text{ mmol g}^{-1} \text{ min}^{-1}$ and a swing size of $1.9 \times 10^{-1} \text{ mmol g}^{-1}$. The membrane was approximately half the rate and capacity of the active component, which agrees with the membrane being approximately 50% active resin and 50% inactive polypropylene.

A necessary first step in using this material is first hydrating it and then drying it; this makes it porous and allows air to pass through. The polypropylene binder swells during this hydration/dehydration preparation, but this has little to no permanent effect on the resin. Subsequent humidity swings have no observable impact on the polypropylene binder.

⁶ [US8083836B2 - Method and apparatus for extracting carbon dioxide from air - Google Patents](#)

⁷ [Excellion Ion-Exchange Membrane for a variety of uses](#)

⁸ <https://patents.google.com/patent/US6503957B1/en>

⁹ [Reversible CO2 capture with porous polymers using the humidity swing - Energy & Environmental Science \(RSC Publishing\)](#)

¹⁰ <https://www.rsc.org/suppdata/ee/c2/c2ee24139k/c2ee24139k.pdf>

The Two-Stage Moisture Swing Cycle

Dry Resin (Absorption)

During this stage, CO_2 is taken up by two mechanisms, according to the graphical abstract of Prof. Wang's paper. These mechanisms involve either the hydroxide (OH^-) or the carbonate (CO_3^{2-}) anions that are mobile in the resin and that counteract the charge of the quaternary ammonium cations, keeping everything neutral. Specifically:

- 1) The **OH- form of absorption** involves the take up of CO_2 by an OH^- group on the amine, turning that group into a bicarbonate group (HCO_3^-).
- 2) The **CO_3^{2-} form of absorption** involves two nearby amines that share a bicarbonate group. The addition of both CO_2 and a free water molecule (H_2O) then yields two separate bicarbonate groups, one per amine. One of these bicarbonates was there before, the other results from the $\text{CO}_2 + \text{H}_2\text{O}$ added.

The dry condition does not require 0% relative humidity, and actually there are reasons to have some humidity - it prevents the formation of urea which will deactivate the sorbent. Even in the "dry" condition there is still about 20% relative humidity.

Wet Resin (Desorption)

During desorption, neighboring amines both with separate bicarbonate groups join together through the loss of one of those bicarbonates. This leaves a carbonate ion and releases $\text{CO}_2 + \text{H}_2\text{O}$, the exact reverse of the CO_3^{2-} form of absorption.

A relative humidity of 95% is sufficient to be considered "wet."

Summary: Under dry conditions, bicarbonates are favored and allow CO_2 capture. Under wet conditions, carbonates are favored, which leads to the release of CO_2 .

CO_2 is initially taken up by OH^- groups on each amine to form bicarbonate groups on those amines. Neighboring amines with bicarbonates are the storage form of CO_2 in dry conditions, and any carbonate ions joining two neighboring amines that are left over from the wet desorption stage are split up by the addition of CO_2 and H_2O to form another bicarbonate so the amines both have their own bicarbonates. When wet, neighboring amines with bicarbonates condense. One bicarbonate goes into releasing CO_2 and H_2O while the other bicarbonate becomes a carbonate that joins the two amines.

Important Characteristics for Moisture Swing Sorbents

High Humidity Function: According to the patent application, a strong base ion exchange resin with a strong humidity function is needed. The latter was described as being able to take up CO₂ as humidity is decreased and give it up as humidity is increased.

Maximum Temperatures: The patent application referenced by Wright and Lackner for the manufacturing process of the resin beads states that one should never exceed 195 degrees F (not Celsius) for anion exchange resin, to preserve chemical stability.¹¹ For cation exchange resin this temperature is higher, 285 degrees F, but anion exchange resin was what was used with quaternary ammonium functional groups to balance the charges and maintain neutrality.

Output CO₂ concentrations between 3-10% were said to be reachable, and close to 100% if the system is completely evacuated/dehydrated (i.e. described as CO₂ becoming a gas and no liquid media being brought in contact with the collector material).

Note: Since CO₂ can be desorbed both in gaseous phase and as a bicarbonate ion, mechanisms that precipitate carbonates such as CaCO₃ from bicarbonate are a way that CO₂ can be sequestered in mineralized form. One such mechanism is the use of calcareous algae, as described in the patent application by Wright and Lackner.

Part 2: On the Use of Amines for CO₂ Removal

A Primer on Amines

All amine groups are chemical bases that contain nitrogen and hydrogen, and are named according to how many of the three hydrogens are replaced by organic chemical groups (substituents). The primary amine has one substituent and 2 hydrogen atoms. The secondary amine has two substituents and one hydrogen atom. The tertiary amine has 3 substituents and no hydrogen atoms.

Closely related is the quaternary ammonium cation, which effectively has 4 substituents. Since four is more than the three bonding sites a nitrogen atom has, this is a cation (i.e. carries a positive charge).

- Primary amines include most amino acids as well as methylamine and ethylamine.
- Dimethylamine and diethylamine are secondary amines while trimethylamine, triethylamine, and EDTA are examples of tertiary amines.

¹¹ <https://patents.google.com/patent/US6503957B1/en>

- The quaternary ammonium cation can be prepared by alkylating tertiary amines with a halocarbon. This takes the tertiary amine and adds a 4th substituent to it.

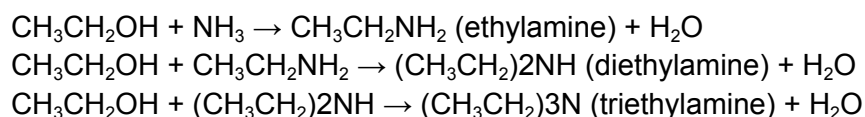
A few amines that have been used in CO₂ removal include monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA).

Amines are ideally purchased from laboratory suppliers, though amines incorporated within anion exchange resins are somewhat expensive. Such examples like Amberlite IRA-900(Cl)¹² have been suggested to work under moisture swing conditions, but have not been tested yet to confirm that.

If you do not have access to a laboratory supplier but do have practical chemistry knowledge, skills, and appropriate resources for mixing and disposal, the content that follows in this section may be useful to you. However, if you will be working with amines purchased from a laboratory supplier, please skip this section and continue with the next.

Amine Synthesis

There are several means of producing amines, with perhaps the most accessible method for an open hardware/open laboratory setting being the alkylation of ammonia with alcohol.¹³ This involves the following reaction: $\text{ROH} + \text{NH}_3 \rightarrow \text{RNH}_2 + \text{H}_2\text{O}$ where R is an alkyl group and OH indicates an alcohol group. Common alcohols are ethyl alcohol (ethanol) and isopropyl alcohol. However, this reaction tends to yield a non-selective mixture of amine products that are primary, secondary, and tertiary. For example, with ethyl alcohol and ammonia we get a non-selective mixture of ethylamine, diethylamine, and triethylamine.¹⁴ Reaction conditions are 150-220 degrees C (not Fahrenheit) in the presence of a silica or alumina supported nickel catalyst, or at 350 degrees C in the presence of aluminum oxide (which can be found on the surface of any aluminum exposed to air, such as aluminum foil). The following reactions will take place under these conditions:



Care should be taken to ensure adequate ventilation at all times. Do not breathe in ammonia fumes as this can result in adverse respiratory effects.¹⁵

¹² [Amberlite™ IRA-900\(Cl\), ion exchange resin, Thermo Scientific™](#)

¹³ <https://www.vanderbilt.edu/AnS/Chemistry/Rizzo/Chem220b/Ch22.pdf>

¹⁴ <https://www.masterorganicchemistry.com/2017/05/26/alkylation-of-amines-is-generally-a-crap-reaction/>

¹⁵ [Adverse respiratory effects in rats following inhalation exposure to ammonia: respiratory dynamics and histopathology](#)

Amines can also be prepared using alkyl halides instead of alcohols, but the use of alcohols are preferred as they are cheaper and their use does not produce salts (i.e. halides) that require disposal.

Amino acid breakdown also releases amines, such as trimethylamine which is produced by fish decay.

Syntheses to Avoid

To underscore the general inaccessibility of amine synthesis in an open hardware/open laboratory setting, the following are syntheses that should not be carried out due to their toxicity or danger.

The methylamines can be produced from alkylation of ammonia with methanol. While the preparation of methylamine, dimethylamine, and trimethylamine are important industrial syntheses, methanol itself is toxic and thus the synthesis of methylamines should be avoided.

The ethanolamines are not the same as the ethylamines. Ethylamine has an ethyl group attached to the nitrogen whereas ethanolamine has an ethyl alcohol group attached. While ethanolamine (as monoethanolamine) has been used to remove CO₂, it is produced by reacting ethylene oxide with ammonia. While ethylene oxide is produced by oxidizing ethylene in the presence of a silver catalyst, and ethylene is a basic plastic monomer that is highly valuable and plentiful (i.e. it is sourced from mostly fossil fuels but also biological sources to make polyethylene), ethylene oxide itself is a very hazardous and reactive gas.

Lastly, ammonia alkylation with any chlorine-containing compound should be avoided because such a reaction (i.e., ammonia with bleach which contains sodium hypochlorite) will yield chloramine gas.¹⁶ Though it is an amine that is found at relatively low levels in the tap water of many municipalities in the United States, chloramine is highly toxic and dangerous.

Now that we've covered what should not be done, Part 2 will examine what we can do instead in an open hardware/open laboratory environment to achieve moisture swing CO₂ removal.

¹⁶ <https://www.healthline.com/health/bleach-and-ammonia#safety-tips>

Part 3: Toward Greener, More Accessible Moisture Swing Materials

Carbon Black

One of the simplest ways to create a moisture swing material was mentioned as functionalizing a high surface area material with polymers containing quaternary ammonium cations and hydroxide anions.¹⁷ Carbon black is a material well suited for this, with a tested surface area of $223 \text{ m}^2 \text{ g}^{-1}$. After a polymerization process to add a hyperbranched styrene-based polymer that could be quaternized with trimethylamine and ion exchanged to convert it to the hydroxide form, the specific surface area was reduced to $21 \text{ m}^2 \text{ g}^{-1}$. This was because the polymer was filling in the pores of the carbon black. Still, despite the surface area reduction, the material had a 3x faster rate of CO_2 sorption compared to the Excellion membrane and a swing size similar to the Excellion membrane. This was even though the material was composed of 50% active material and 50% carbon black.

To learn more about how to functionalize carbon black, this paper¹⁸ describes the polymer grafting process in greater detail. It is a highly organic chemistry-intensive process and thus not the one recommended.

Quaternized Biochar

A precedent for the synthesis of quaternized biochar was set in a 2021 paper¹⁹ by Bei Wang *et al.* (different from Tao Wang). Biochar has a similar to higher specific surface area than the carbon black specified above, ranging from 250 to over $1000 \text{ m}^2 \text{ g}^{-1}$. Compared to carbon black, which is made from fossil fuels at extremely high temperatures,²⁰ biochar is itself a form of carbon storage and has the added benefit of having a much easier functionalization.

The only reagents that were used in the above paper for functionalization were: K_2CO_3 , HCl, isopropyl alcohol, ZnO nanoparticles, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, betaine, and graphite paper. Of these, only the betaine appears necessary for quaternizing the biochar for CO_2 removal uses. The mesoporosity-associated reagents described in the next paragraph do add value, but only if preparing the biochar from raw material. Such preparation requires pyrolysis equipment and subsequent grinding, whereas it is likely more cost-effective to purchase fine biochar.

¹⁷ [Reversible CO2 capture with porous polymers using the humidity swing - Energy & Environmental Science \(RSC Publishing\)](#)

¹⁸ [Carbon black functionalized with hyperbranched polymers: synthesis, characterization, and application in reversible CO2 capture - Journal of Materials Chemistry A \(RSC Publishing\)](#)

¹⁹ <https://www.sciencedirect.com/science/article/pii/S1385894721011724>

²⁰ [AP-42. CH 6.1: Carbon Black](#)

The mesoporosity-associated reagents are the ZnO, K₂CO₃, and HCl. The ZnO nanoparticles were used to help form the mesoporous biochar prior to biochar creation. K₂CO₃ was also used to increase the specific surface area prior to biochar creation. The HCl (2 mol/L) was used after the biochar underwent cooling and grinding to remove impurities (leftover Zn nanoparticles after ZnO is reduced to Zn) while the mixture of HCl and biochar was heated for 24 hours. The biochar then needed washing several times with ultrapure water until a neutral solution resulted and no chloride ions could be detected.

Once the biochar is cool and clean enough, it is impregnated with betaine at a mass ratio of 1:2, then stirred at 40 degrees C for 12 hours. Betaine is a necessary reagent for quaternization to yield quaternary ammonium functionalized biochar. It is a modified amino acid consisting of glycine with three methyl groups²¹ and thus is on the federal GRAS (Generally Recognized as Safe) list under number 4223.²² It is available on Amazon in 0.5 kg (1.1 lb) containers for \$15.95 each²³ with discounts at higher quantities. It is itself a quaternary ammonium compound,²⁴ thus its inclusion within biochar will provide it with the necessary CO₂ absorption/desorption functionality.

The isopropyl alcohol is only needed for preparation of biochar electrodes to make a solution along with the Al(NO₃)₃ · 9H₂O, the latter of which is needed only to improve the adhesion and deposition rate between colloidal particles and electrodes. Since we do not need to make electrodes for our CO₂-absorbing sheets, both these reagents are unnecessary.

Suggested Moisture Swing Method

General instructions are as follows for a method that could be tested as a next step.

Quaternization: Finely powdered biochar (example characteristics: <50 mesh or <297 microns, with a surface area of 415 m² g⁻¹) at room temperature should be mixed with betaine (specifically glycine betaine, which is trimethylglycine) at a mass ratio of 1:2, using a minimal amount of distilled water (non-chlorinated) at an approximate rate of 1 ml per g biochar. Use more distilled water if needed to make a somewhat thick mixture of dissolved betaine and biochar. Then stir at 40 degrees C for 12 hours. Afterward, do not rinse - instead, let dry.

Ion exchange: This step may help improve the swing size in case there are Cl⁻ ions transferred over from the biochar during the quaternization step. The biochar might benefit from previous washing with a carbonate such as washing soda, Na₂CO₃ or a hydroxide such as NaOH. Such

²¹ [Betaine | C5H11NO2 - PubChem](#)

²² <https://www.femaflavor.org/sites/default/files/22.%20GRAS%20Substances%20%284069-4253%29.pdf>

²³ [Amazon.com: Nutricost Betaine Anhydrous Trimethylglycine \(TMG\) Powder 500 Grams : Health & Household](#)

²⁴ [A reliable method for spectrophotometric determination of glycine betaine in cell suspension and other systems](#)

washing is described here²⁵ as biochar pretreatment and activation and is something that can be experimented with to determine if it improves CO₂ absorption capacity.

Sheet formation: Embedding the resulting mixture in any polymer will occlude the pores and reduce perhaps half of the surface area. As an alternative that will prevent occlusion, biochar can be made magnetic through the incorporation of transition metals and their oxides,²⁶ to allow for easy separation from a magnetic sheet or other magnetizable surface as needed. The magnetic materials will of course take up room that would otherwise be taken up by the betaine, thus reducing the effectiveness of the sheet at CO₂ capture. Thus, for a first try, the dry quaternized biochar should be adhered to the front and back of a double-sided adhesive sheet. The adhesive must not be water-soluble. Excess biochar should be placed on the sheet, pressed down, then the sheet should be vigorously shaken to remove non-adhered biochar. For greater sheet stiffness, two such adhesive sheets can be adhered to the front and back of a third sheet that provides the required degree of stiffness.

What is expected:

Absorption: When dry, CO₂ is expected to absorb onto the betaine.

Desorption: When the sheet is wetted, the CO₂ should be released from the betaine.

CO₂ Release Test

It is known that CO₂ dissolves in water to form carbonic acid, lowering the pH. Thus, pH can be used as a proxy to coarsely determine whether CO₂ has been captured and is being released.

1. Take 300 ml of distilled water and measure its pH.
2. Pour 100 ml of that distilled water into each of three sandwich-sized plastic reclosable bags (i.e. Ziploc bags).
3. Flatten all bags to let out the air, close it, and set one of these aside. This will be the water control bag.
4. To the second bag, add a 5x5 cm square of biochar sheet that has been exposed to dry air (< 25% relative humidity) for at least 24 hours. This will be the biochar control bag. The biochar sheet should have been prepared in the same manner as the quaternized biochar sheet, with the exception of adding any quaternized material.
5. Quickly flatten the bag to let out the air, then close the bag. Gently turn the bag so that water washes over the sheet for 15 seconds, then let the bag lie flat. Observe the bag for any appearance of bubbles on the sheet, then withdraw 50 ml of water to do a pH test. Then flatten the bag to let out the air, then close the bag and let sit for 10 minutes.
6. To the third bag, add a 5x5 cm square of quaternized biochar sheet that has also been exposed to dry air (< 25% relative humidity) for at least 24 hours.

²⁵ [A critical review on biochar-based engineered hierarchical porous carbon for capacitive charge storage - ScienceDirect](#)

²⁶ [Magnetic biochar for environmental remediation: A review - ScienceDirect](#)

7. Quickly flatten the bag to let out the air, then close the bag. Gently turn the bag so that water washes over the sheet for 15 seconds, then let the bag lie flat. Observe the bag for any appearance of bubbles on the sheet, then withdraw 50 ml of water to do a pH test. Then flatten the bag to let out the air, then close the bag and let sit for 10 minutes.
8. At 10 minutes, observe all three bags for the presence of bubbles on the sheet, if the bag contains a sheet.
9. Open the water control bag and measure the pH of the water in that bag.
10. Open the biochar control bag, remove the biochar sheet, and set it aside to dry. Then measure the pH of the water in that bag.
11. Open the quaternized biochar bag, remove the sheet in that bag, and set it aside to dry. Then measure the pH of the water in that bag.
12. If there was a significant decrease in the water's pH and small but slowly growing bubbles were observed on the sheet prior to pH testing, this likely indicates that captured CO₂ was released. This test should be followed by a more precise testing method.

Sample Expected Results

	Water Control	Biochar Control	Quaternized Biochar
pH of initial distilled water (step 1)	7	8.5	8.5
Bubbles present after 15-second water wash?	no	no	maybe
pH of water from bag after 15 seconds	7	8.5	< 8.5
Bubbles present after 10 minutes in water?	no	no	yes
pH of water in bag at 10 minutes	7	8.5	< 8.5

Additional Supporting Literature

Betaine has been used with biochar for the removal of phosphate in aqueous solutions.²⁷

²⁷ [Benign zinc oxide betaine-modified biochar nanocomposites for phosphate removal from aqueous solutions - ScienceDirect](#)