

THE UNIVERSITY OF CHICAGO

EXPERIMENTAL DEVELOPMENT OF PASSIVE AND HIGH-CONTACT
PHOTOTHERMAL SYSTEMS FOR CARBON CAPTURE

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BY
KATIE KLOSKA

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For my parents

It always seems impossible until it's done. Nelson Mandela

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Abstract

As global efforts to mitigate climate change intensify, developing carbon capture technologies that are both energy-efficient and scalable is paramount. This dissertation presents the design, development, and evaluation of two novel photothermal carbon capture systems aimed at using solar energy to regenerate CO₂-rich solvent solutions: the Passive Photothermal Capture (PPC) device and the High-Contact Photothermal (HCP) device. The PPC system combines a light-transmissive window, a hydrophobic gas-permeable membrane, and a carbon-black amine nanosolution to enable CO₂ regeneration with minimal external energy input. Lamp and sunlight-based experiments demonstrate regeneration efficiencies up to 4.4 mol CO₂/MJ, with techno-economic analysis highlighting key cost drivers such as solvent volume and CO₂ compression. The HCP system builds on these principles using hollow fiber membrane contactors (HFMCs) to maximize gas-liquid contact surface area and employs nanoparticle-assisted photothermal heating for solvent regeneration. While preliminary testing of HCP components showed successful regeneration under thermal heating, integrated photothermal operation was hindered by nanoparticle aggregation, prompting further investigation into stabilization strategies. Together, these proof-of-concept systems demonstrate the potential of solar-driven photothermal regeneration for both point-source and direct air carbon capture applications, offering pathways toward more sustainable and decentralized CO₂ removal technologies.

1 Introduction

1.1 Carbon Capture

The Intergovernmental Panel on Climate Change (IPCC) has stated that the transition to clean energy alone will be insufficient to meet our climate goals (1). While aggressively decarbonizing our energy grid through the widespread adoption of renewables like wind, solar, geothermal, and nuclear power is crucial, it will not fully mitigate the climate crisis. Hard-to-abate sectors, such as cement, steel, and heavy transport, will continue to generate significant emissions even with ambitious decarbonization efforts (2). Consequently, carbon removal strategies are increasingly recognized as essential for offsetting residual emissions and preventing global warming from exceeding the 1.5°C threshold.

A significant amount of CO₂ has already accumulated in the atmosphere due to over a century of industrial activity, leading to global warming. Even if we completely cease emissions from traditional fossil fuel sources, the existing atmospheric CO₂ concentration will continue to trap heat. Certain critical sectors of the economy, such as cement, steel, glass, chemicals, and heavy transportation, are inherently difficult to decarbonize. These "hard-to-abate" sectors will continue to emit substantial amounts of CO₂, posing a significant challenge to achieving our climate goals.

The accumulation of CO₂ in the atmosphere demands action. Decarbonization efforts must encompass a diverse range of technologies, including not only developing renewable energy

technologies and energy storage solutions but also reliable carbon capture, utilization, and storage (CCUS) technologies.

Successfully decarbonizing hard-to-abate sectors, such as those in the industrial and fossil fuel industries, requires “point source capture” systems that prevent CO₂ emissions from entering the atmosphere directly from industrial flue gases (3). This approach differs significantly from “direct air capture” (DAC), which captures CO₂ from ambient air, where the concentration is significantly lower (around 0.04% compared to up to 30% in flue gases) (4). A useful analogy for distinguishing between point-source carbon capture and direct air capture (DAC) is to imagine atmospheric CO₂ as a bathtub being filled with water. Point-source capture is like turning off the faucet—preventing new emissions from entering the system. In contrast, direct air capture functions like pulling the drain plug—removing CO₂ that has already accumulated in the atmosphere. While both are necessary to stabilize global CO₂ levels, DAC is particularly important for addressing legacy emissions and achieving net-negative targets.

1.1.1 Point Source Capture

Point source capture refers to the direct integration of carbon capture technology into industrial flue gas streams, enabling the reduction or elimination of CO₂ emissions from manufacturing processes. In steel production, for example, flue gas typically consists of 20% CO₂, 25% CO, 3% H₂, and 52% N₂ (5). Point source capture systems use chemical or physical methods to selectively separate CO₂ from these gas streams, and reduce the net carbon emissions of the process. The captured CO₂ is then compressed and either used in value-added products or

sequestered underground for permanent storage. This work will concentrate solely on the carbon capture separation step within the context of carbon capture systems, excluding the transportation, storage, and utilization aspects of CCUS.

To date, popular technologies for capturing CO₂ from flue gas streams include metal organic frameworks, membrane based systems, and liquid capture (6) . Among these technologies, liquid capture, specifically aqueous-amine-based capture, has been considered a promising near-term solution for CO₂ capture from flue gas because of its fast absorption rate, high CO₂ selectivity, high CO₂ absorption and regeneration ability (7).

However, wide implementation of aqueous amine capture is hindered by the high cost associated with the parasitic energy consumption during solvent regeneration (8). Solvent regeneration typically occurs in a reboiler where the bulk capture solution is heated up to 150C by hot steam at the bottom of the regeneration column. The heat required for this process is known as regeneration reboiler heat duty, which can constitute over 50% of the energy required for aqueous-amine based carbon capture (9).

1.1.2 Direct Air Capture

Direct air capture (DAC) refers to carbon capture methods which draw down CO₂ emissions from ambient air. We can compare the process to point source capture by first looking at the order magnitude difference between CO₂ concentrations in air versus flue gas streams. In flue gas streams, CO₂ is present at up to 300,000 ppm (meaning for every one million gas molecules,

300,000 of those are CO₂ molecules). In ambient air, CO₂ is present at 400 ppm (meaning for every one million air molecules, 400 of those are CO₂ molecules). Because of this, to be effective, direct air capture must do a much better job at selecting specifically for CO₂ molecules and drawing a lot of air into separating equipment. The process of doing this drives energy requirements for DAC up. Energy requirements for DAC are 4-6 times the energy consumption of point source (10).

Today's leading DAC technologies capture CO₂ using either synthetic solid sorbents or liquid sorbents. In these systems, fans draw air through large contactors where CO₂-reactive chemicals, such as amines or hydroxides, facilitate capture. The contactors are designed with structured materials that regulate airflow, ensuring sufficient residence time for CO₂ to interact with the capture medium. Amines react with CO₂ to form carbamate bonds, while hydroxides form carbonate bonds (11). To recover the captured CO₂, these bonds are broken through heat, pressure swings, or chemical displacement reactions, after which the CO₂ is compressed for transportation and storage (12).

Solid sorbents, while capable of regenerating at relatively low temperatures (80–120°C), require near-vacuum conditions to release CO₂, which is highly energy-intensive. Liquid sorbents, such as hydroxides, on the other hand, demand extremely high temperatures (around 900°C) from high-quality heat sources for regeneration (13). This makes energy consumption a critical challenge for DAC, even more so than for point source capture, where CO₂ concentrations are much higher but energy demands remain a key consideration. These energy demands create a

significant challenge for DAC, which raises concerns about grid flexibility and the feasibility of integrating these systems into existing energy infrastructure.

Most direct air capture (DAC) companies aim to avoid using fossil fuels by powering their systems with renewable energy. While this reduces emissions, it also introduces several challenges. Some DAC technologies require high-temperature heat—for instance, those relying on calcination in kilns—which makes them difficult to electrify or pair with intermittent renewable sources (14). Although efforts are underway to develop electric kilns, many systems still rely on natural gas. On the other hand, DAC technologies that operate at lower temperatures and can run on electricity (such as pressure swing systems) face the issue of opportunity cost: using renewable energy for DAC may divert it from more cost-effective decarbonization strategies, like electrifying transportation. A 2021 analysis, for example, showed that powering electric vehicles with renewables achieves greater CO₂ reductions per unit of energy than using the same power for DAC (15).

These high energy demands pose significant challenges for integrating DAC into existing energy infrastructure. They raise concerns about grid stability and highlight the need for flexible, efficient systems. Moreover, the need for large-scale renewable generation—either on-site or nearby—increases the physical and financial footprint of DAC plants, making siting and cost even more complex.

Additionally, the high energy requirements influence the overall footprint of the plant, as larger facilities may be needed to accommodate on-site renewable generation or alternative energy

sources to avoid reliance on fossil fuels. This further complicates siting decisions and cost considerations. As a result, energy efficiency—or designing systems that avoid competing for limited renewable energy—becomes a critical consideration for scaling DAC sustainably.

1.1.3 Transportation Constraints and the need for energy flexibility

There are currently 15 operational commercial CCS projects in the U.S., with a total storage capacity of just 21 million tons of CO₂—roughly 0.34% of national emissions (16). Despite growing momentum, early-stage carbon capture companies are struggling to gain public support and navigate state and local permitting processes, particularly when it comes to building out the CO₂ transport infrastructure required to link capture plants with storage sites.

Take, for example, Summit Carbon Solutions, which aims to construct a multi-state pipeline network to connect more than 30 ethanol plants in the Midwest to underground storage sites in North Dakota (17). Despite extensive partnerships, both North Dakota and South Dakota initially denied permits for the pipeline, citing a lack of landowner support, inability to comply with local ordinances, and potential environmental impacts (18). Similarly, Navigator CO₂ Ventures abandoned a proposed pipeline project meant to capture and transport 15 million metric tons of CO₂ annually, due to persistent regulatory hurdles (19).



Figure 1 Summit Carbon Solutions Proposed CO₂ transportation routes (20)

These projects underscore a key challenge: CO₂ transport, especially via pipeline, is logistically complex, capital-intensive, and politically fraught. Costs vary, but most integrated assessment models estimate transport and storage at around \$10/tCO₂, with some projections falling between \$5–\$15/tCO₂ (21). However, pipeline capital costs alone can reach billions, and repurposing existing infrastructure is not always viable—CO₂ must be transported at higher pressures than natural gas, requiring purpose-built, thick-walled pipelines (22).

Shipping CO₂, as exemplified by the Northern Lights project in Europe (23), may be a more flexible alternative, with costs less sensitive to distance and lower capital intensity. However, ship-based transport is only feasible at scale and near coastal storage infrastructure—limiting its applicability in most U.S. inland regions.

We can also compare current CCS project locations to the emerging map of county-level potential for adsorbent-based Direct Air Capture (DAC) deployment. This map identifies an area of high-potential sites across the U.S. that are selected based on two primary criteria: (a) close proximity to geologic CO₂ storage reservoirs and (b) abundant excess wind and solar energy availability. Notably, these high-potential counties do not overlap well with the current distribution of CCS projects, which are largely co-located with industrial point sources.

Beyond energy and storage compatibility, climate factors such as temperature and humidity can influence DAC and point-source feasibility and system design. For solvent-based systems, hotter and drier climates increase water losses due to solvent evaporation during air contact. In contrast, hot and humid conditions can enhance capture efficiency, potentially increasing rates by 10–15% with a 10°C rise in temperature (24). Adsorbent-based DAC systems are also affected by these environmental factors, especially because they operate on sub-hourly cycles. Diurnal and seasonal variations in humidity and temperature can cause swings in performance by a factor of two, making climate-aware siting critical to system efficiency and consistency.

These logistical and economic barriers point to a major limitation of today's CCS and DAC projects: most are sited based on industrial emission sources and energy infrastructure rather than proximity to storage. Current capture facilities are largely tied to ethanol, ammonia, and hydrogen production in the Midwest and Gulf Coast, while the most favorable and cost-effective CO₂ storage sites are scattered more broadly—including underutilized basins in places like the

Gulf of Mexico, Kentucky, and parts of the Rockies (25). This is where energy-efficient, location-flexible carbon capture systems can offer a critical advantage.

If a DAC or point-source system does not rely heavily on grid-tied renewable energy—or requires less overall energy input—it no longer needs to be co-located with industrial plants or energy infrastructure. Instead, it can be deployed strategically near low-cost CO₂ storage sites, dramatically reducing or even eliminating transport requirements. This could bypass the regulatory issues and capital expense of pipeline buildouts altogether. It also allows for siting in areas where community support and permitting are more favorable.

1.1.4 Technoeconomic Analysis of Carbon Capture technologies

As carbon capture technologies continue to advance, it is critical to evaluate their feasibility not only from a technical perspective but also from economic and environmental standpoints. Two key methods that can be used to evaluate this are Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA) (26). These frameworks help assess the cost-effectiveness, scalability, and overall environmental impact of engineered systems, providing essential insights for both researchers and industry stakeholders.

Techno-Economic Analysis (TEA) is a systematic approach to evaluating the economic viability of a technology by integrating technical performance metrics with cost considerations. In the context of carbon capture, TEA assesses capital expenditures (CAPEX), operational expenditures

(OPEX), energy consumption, and overall process efficiency to estimate the cost per ton of CO₂ captured (26).

TEAs are particularly useful in comparing different carbon capture technologies, such as solvent-based capture, solid sorbents, and membrane-based separation, by quantifying trade-offs between performance and cost. These analyses can also incorporate sensitivity studies to understand how variations in energy prices, material costs, or policy incentives impact the overall financial feasibility of a given capture system.

One of the primary goals of TEAs in carbon capture is to determine whether a system can be scaled from laboratory or pilot-scale operations to commercial deployment. TEAs help identify key cost drivers—such as solvent regeneration energy, compression requirements, and infrastructure investments—that influence the total cost per ton of CO₂ removed. Additionally, TEAs can compare different capture scenarios, such as direct air capture (DAC) versus point-source capture, to determine which approach is more economically viable under specific conditions.

1.1.5 Current Issues Facing Carbon Capture Technologies

Carbon capture has progressed to the deployment stage in recent years, driven by growing interest in climate mitigation strategies. Increased government and private sector support has accelerated funding, development, and scaling efforts for these technologies. Despite substantial investments in engineered direct air capture (DAC) systems—such as Carbon Engineering,

Climeworks, and Heirloom—and in point-source capture systems—such as Shell’s Quest Carbon Capture and Storage (CCS) facility, Aker Carbon Capture, and LanzaTech—these technologies still face significant challenges that hinder widespread adoption.

One of the primary challenges of carbon capture is the high energy demand required for CO₂ separation, regeneration, compression, and transportation. Shell’s Quest CCS facility, for example, captures CO₂ from process gases in three steam methane reformers using Shell’s ADIP-X amine-based solvent technology. While this process successfully achieves a CO₂ purity of 99%, it requires significant thermal energy for solvent regeneration, increasing overall facility emissions and operational costs (27) (28).

Aker Carbon Capture (29) offers a modular amine-based capture solution designed for industrial applications, yet it faces similar energy consumption issues. Amine-based capture is effective at separating CO₂ from flue gases, but the high regeneration temperatures (typically 100–150°C) demand substantial heat input. This can be particularly challenging for industries without readily available waste heat or low-carbon energy sources, leading to increased reliance on fossil fuels for process heating. Additionally, amine degradation over time generates waste products that require disposal, adding to operational complexity and costs.

Direct air capture systems face even greater energy challenges due to the low concentration of CO₂ in ambient air. Carbon Engineering employs a liquid hydroxide-based approach that captures CO₂ through a series of chemical reactions and requires temperatures of around 900°C for regeneration (30) (31). This necessitates a high-quality heat source, often from natural gas,

which can offset some of the climate benefits unless coupled with renewable energy. The large energy demand raises questions about grid integration and whether DAC can be scaled affordably without straining clean energy resources.

Similarly, Heirloom utilizes mineralization, where naturally occurring minerals absorb CO₂ from the air (32). While this passive process reduces energy demands for capture, the calcination step for regenerating minerals requires high temperatures, similar to Carbon Engineering's approach. This heat demand presents a major barrier to cost reduction and scalability, as sourcing low-carbon, high-temperature heat remains a challenge. Additionally, Heirloom's process is constrained by the availability of suitable minerals and the logistics of large-scale mineral processing.

Beyond energy consumption, carbon capture technologies also face infrastructure and scalability challenges. Effective deployment requires extensive integration with existing industrial processes, dedicated CO₂ transport pipelines, and secure storage sites. Compression and transportation of CO₂ add further costs, as most storage reservoirs are located far from major emission sources, necessitating high-pressure transport, which can be a major operational expense. Additionally, the large physical footprint of DAC plants poses a logistical challenge, as scaling to meaningful levels of CO₂ removal requires vast amounts of land and sorbent material.

Economic feasibility remains a major hurdle, as the cost per ton of CO₂ captured varies widely depending on the technology, CO₂ concentration, and system configuration. Current estimates place capture costs between \$100 and \$600 per ton for DAC (33), while point source capture

systems range from \$15 to \$130 per ton (34) (35). However, these estimates often exclude hidden costs such as maintenance, solvent losses, and compression, which can significantly increase the true cost of deployment. Furthermore, uncertainty around long-term policy incentives, carbon credit pricing, and regulatory support complicates investment decisions for large-scale capture projects.

While these challenges present obstacles to widespread adoption, continued advancements in solvent efficiency, process integration, and energy sourcing could help lower costs and improve feasibility. Innovations in heat recovery, alternative sorbents, and modular system design offer promising pathways for reducing energy consumption and capital costs. Additionally, policy support, such as carbon pricing and tax incentives, will play a crucial role in determining the pace at which carbon capture technologies can scale to meet global climate targets.

1.2 Nanoparticles and Photothermal Heating

A major hurdle to scaling carbon capture technologies is the energy intensity of solvent regeneration, which can account for up to 80% of the total energy demand in conventional CCS systems (36) (37). To lower the costs associated with solvent regeneration, our group has demonstrated a method for regenerating CO₂ capture fluids using actinic light and light-absorbing nanoparticles of carbon black (NCBs), which lowers the bulk temperature required for regeneration by as much as 50C (38). Additionally, instead of using traditional bulk heating methods, NCBs allow the thermal requirements of the system to be satisfied solely by photothermal energy from sunlight.

1.2.1 Bulk Heating

Amine scrubbing with thermal regeneration remains the benchmark method for carbon dioxide (CO₂) capture, especially from fossil fuel combustion sources (36). This post-combustion process relies on chemical absorption followed by thermal desorption: CO₂ is absorbed from flue gas using an amine-based solvent in an absorber column, typically operated between 40–70 °C. The CO₂-rich solvent is then routed to a stripping column, where it is regenerated using bulk heating to 100–150 °C, usually via steam, releasing purified CO₂ gas for compression or storage.

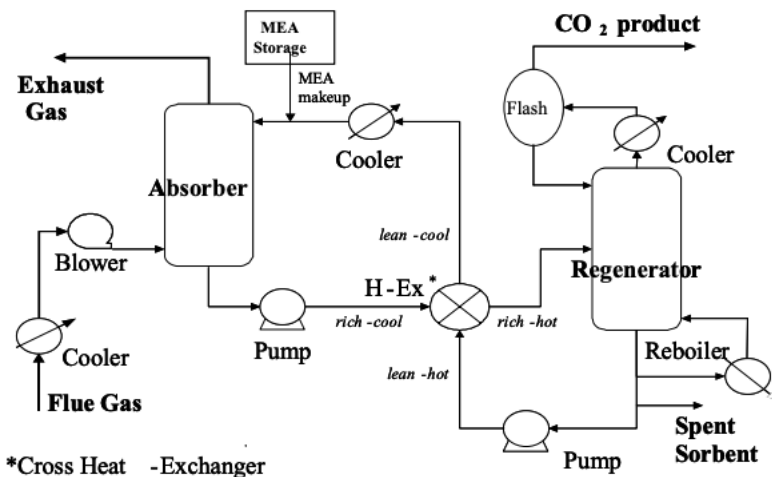
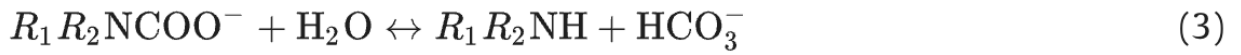
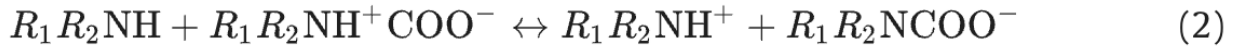


Figure 2 Flowsheet for CO₂ capture from flue gases using amine-based systems (39)

Aqueous amine solvents operate via well-established reaction pathways. Primary and secondary amines such as monoethanolamine (MEA) and 2-(methylamino)ethanol (MMEA) are commonly used due to their high reactivity and fast absorption kinetics. These amines react with CO₂

through a two-step mechanism: (1) formation of a zwitterion, followed by (2) proton transfer to form a carbamate (40) (41). This mechanism, while efficient, also limits theoretical CO₂ loading to 0.5 mol CO₂ per mol amine, as two amine molecules are required per molecule of CO₂.



Among these, MEA (typically used as a 30 wt% aqueous solution) is widely adopted due to its low cost, fast reaction rate, and ease of handling. However, MEA-based capture systems are highly energy-intensive, with solvent regeneration alone accounting for a large share of total energy consumption. This is largely due to the high heat capacity of water in the aqueous system, as well as the enthalpy of the CO₂-amine bond (36) (42).

To reduce desorption energy demands, amine sorbents must ideally combine high CO₂ loading capacity, rapid kinetics, and a favorable heat of absorption. The exothermic absorption process produces a localized temperature increase in the absorber—often called the temperature bulge. In practice, much of this reaction heat is lost through solvent vapor or water knockout, rather than being efficiently reused in the desorber (43) (42). Improving energy recovery and integration between these process steps is crucial for optimizing performance.

Despite these challenges, MEA remains a dominant industrial choice due to its strong performance profile. However, its high regeneration energy remains a major barrier to broader

deployment of carbon capture systems. This energy burden increases operating costs and reduces overall system efficiency. Addressing these challenges—through solvent innovation, alternative regeneration strategies, or process integration—is essential for advancing scalable and cost-effective carbon capture solutions.

1.2.2 Nanoparticles to promote release

To lower the costs associated with solvent regeneration, our group has developed a method that utilizes actinic light and light-absorbing carbon black nanoparticles (NCBs) to lower the bulk temperature required for CO₂ desorption by as much as 50°C. Unlike conventional bulk heating methods, which rely on high-quality thermal energy, NCBs enable solvent regeneration through photothermal energy derived from sunlight, reducing dependence on fossil fuel-based heat sources (44).

Carbon black nanoparticles are highly efficient absorbers of light, capable of generating water vapor when exposed to sunlight. The hypothesized mechanism for this photothermal release begins with the formation of a gas film around each nanoparticle, which acts as an insulating layer due to its lower thermal conductivity. This insulation raises the nanoparticle's surface temperature, allowing the gas film to expand until it reaches the bulk solution surface and is released. Once the gas escapes, the nanoparticle returns to the solution and repeats the process (44)

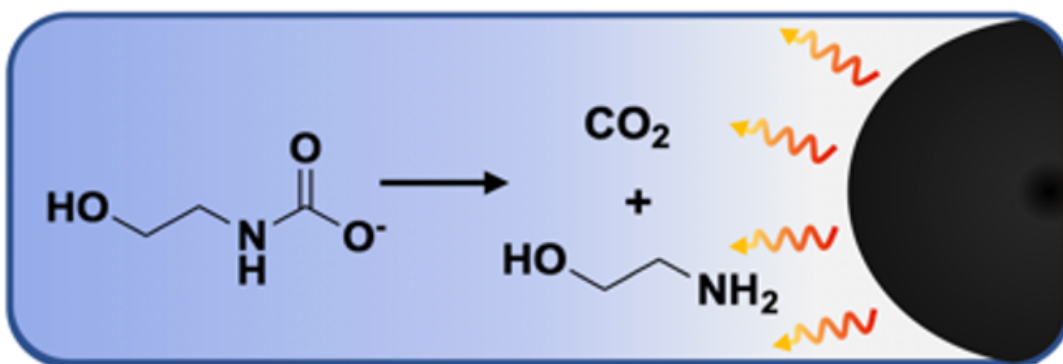


Figure 3 Photothermal heating diagram of nano solutions of aqueous amines (44).

Importantly, this approach is viable in both aqueous and non-aqueous capture systems, including widely used solvents such as MEA. By leveraging solar energy, this method offers a sustainable, decentralized alternative to traditional energy-intensive regeneration techniques, reducing grid dependency and enhancing the feasibility of carbon capture deployment in remote or off-grid locations.

1.3 Sorbents and Solvents and Carbon Capture

The selection of chemistries for CO₂ separation, whether from industrial flue gas or ambient air, is highly dependent on the specific environmental conditions of the feedstock. Factors like temperature, humidity, and the overall gas composition significantly influence the effectiveness of different sorbents. For instance, point-source capture from flue gas presents a unique set of challenges. This gas stream is typically hot, saturated with water vapor, and contains various potentially degrading contaminants. However, its high CO₂ concentration allows for the use of sorbents that prioritize robustness and resistance to fouling over extreme selectivity. These

sorbents must withstand the harsh conditions of flue gas while efficiently capturing the abundant CO₂, a stark contrast to the requirements for dilute ambient air capture.

Conversely, Direct Air Capture (DAC) sorbents face a different challenge: extracting CO₂ from ambient air. While ambient air is relatively free of the complex contaminants found in flue gas, it presents an extremely low CO₂ concentration, typically around 400 ppm. This requires the development of sorbents with exceptionally high selectivity and loading capacity for CO₂. In essence, DAC sorbents must be able to efficiently capture trace amounts of CO₂ from a sea of other gases. To address these demands, various chemical approaches are being explored, each with its own advantages and limitations.

1.3.1 Aqueous Amines

MEA is the most widely studied benchmark sorbent. Its reaction with CO₂ proceeds via a zwitterionic intermediate that rapidly deprotonates to form a stable carbamate. At low CO₂ loading levels (below ~0.32 mol CO₂/mol MEA), carbamate dominates the speciation. As the loading increases (above ~0.5 mol CO₂/mol), carbamate hydrolyzes to form bicarbonate, shifting the absorption mechanism (45). Regeneration occurs through thermal desorption, during which bicarbonate decomposes and carbamate breaks down, allowing MEA to be recycled. While MEA offers rapid kinetics and high cyclic capacity, it also suffers from oxidative degradation, especially under air-rich conditions relevant to DAC (46). These degradation pathways include the formation of nitrosamines and amides, which pose environmental and health concerns and decrease amine efficiency (47).

Alternative amines have been explored to address the limitations of MEA. 2-(methyamino) ethanol (MMEA), a tertiary amine, avoids carbamate formation due to steric hindrance and the absence of an N–H bond, and instead promotes CO₂ hydration to bicarbonate (48).

Diglycolamine (DGA), a primary amine containing ether groups, also forms carbamate species but exhibits improved solubility and reduced volatility. Its reactivity parallels MEA with modestly altered kinetics and stability (49).

Across all aqueous amine systems, water plays a critical role in mediating proton transfer and stabilizing intermediates, directly influencing both absorption and desorption efficiency. Primary and secondary amines typically offer high initial absorption rates and capacities due to strong carbamate binding, but require more energy for regeneration. Tertiary amines, while slower to react, provide lower regeneration energy requirements and can be more stable under DAC-relevant oxidative conditions.

1.3.2 CO₂BOLS

CO₂-binding organic liquids (CO₂BOLs) represent a class of switchable, non-aqueous solvents specifically engineered for reversible CO₂ capture (50). These systems rely on organic bases paired with nucleophilic anions that can directly bind CO₂ without the need for water, circumventing many of the degradation and volatility challenges associated with traditional aqueous amine systems. A representative CO₂BOL, 2-ethyl-1-methylimidazolium phenolate (EEMPA), was developed at Pacific Northwest National Laboratory (PNNL) as a more durable

alternative to amine-based solvents, particularly for applications such as direct air capture (DAC) (51). In 2-EEMPA, the phenolate anion serves as the active binding site, reacting directly with CO₂ to form a reversible phenyl carbonate adduct via nucleophilic attack on the CO₂ molecule.

Unlike aqueous amines, this reaction does not proceed through carbamate formation and does not require water as a proton shuttle, reducing both the complexity of the reaction network and the susceptibility to degradation (52). The bound CO₂ can be released by heating or reducing the partial pressure of CO₂, allowing for solvent regeneration with lower energy input compared to thermal carbamate breakdown. The absence of water also minimizes oxidative degradation pathways that limit the lifetime and efficiency of amine-based systems. CO₂BOLs like EEMPA therefore offer a promising platform for DAC due to their lower regeneration energy requirements, improved long-term chemical stability, and reduced volatility relative to conventional aqueous solvents

1.3.3 Amino Acids

Amino acids are another promising class of sorbents for CO₂ capture due to their hybrid properties. They have similar CO₂ reaction kinetics of amines while exhibiting the low volatility, high thermal stability, and environmental safety of inorganic salts. When neutralized with alkali metals to form amino acid salts, these compounds react with CO₂ via carbamate and bicarbonate formation, similar to conventional aqueous amines, but with significantly enhanced resistance to oxidative degradation and minimal evaporative loss (53) (54).

Their ionic nature and bio-inspired chemistry—mirroring natural CO₂-binding in biological systems—make them particularly well-suited for direct air capture (DAC), where the challenges of dilute CO₂ concentrations and oxygen-rich environments render traditional amines less effective.

Glycine, the simplest amino acid, forms potassium glycinate (Gly-K) upon neutralization. In aqueous solution, the glycinate anion (NH₂CH₂COO⁻) reacts quickly with dissolved CO₂ to form a carbamate intermediate (NH₂CH₂COOCOO⁻), which can further hydrolyze to bicarbonate depending on solution conditions. Under DAC-relevant conditions, Gly-K can achieve a theoretical CO₂ loading of up to 0.8 mol CO₂/mol amino acid (55).

Potassium lysinate (Lys-K), derived from lysine, features two amine groups—an α-amino and an ε-amino group—allowing for dual-site CO₂ reactivity. The ε-amino group is particularly reactive, forming stable carbamate species via carbamylation (56). In functionalized materials such as lysine-modified metal-organic frameworks (MOFs), CO₂ uptake occurs primarily through bicarbonate formation in the presence of moisture, with reversible desorption under mild conditions. This dual-reactivity structure enables higher CO₂ loading potential and increased robustness under humid and oxidative conditions compared to Gly-K (57).

Table 1 Properties of Aqueous Amines, CO₂BOLs, and Amino Acids

Property	Aqueous Amines	CO ₂ BOLs	Amino Acids
CO ₂ Binding	Carbamate	Carbamic Acid	Carbamate/bicarbonate
Regeneration Energy	High ($\Delta H \sim 85$ kJ/mol)	Moderate ($\Delta H \sim 70$ kJ/mol)	Low ($\Delta H \sim 55$ kJ/mol)
Oxidative Stability	Poor	Moderate	High
DAC Feasibility	Limited	Promising (low volatility)	Optimal (crystallization)

1.4 Membrane Characteristics and Characterization

Membranes play a central role in many CO₂ capture technologies, but their function can vary significantly depending on the system design. In most traditional membrane-based CO₂ separation systems, the membrane itself is the active separation medium. These systems use permeable or semi-permeable membranes—such as polymeric membranes, facilitated transport membranes, or mixed-matrix membranes (58)—to selectively transport CO₂ from a gas mixture. Separation performance is driven by differences in gas diffusivity and solubility, with CO₂ ideally permeating faster than other components. Recent advances in these systems include operation at sub-ambient temperatures, hybrid configurations with solvents, and enhanced tolerance to gas contaminants (59) (60). While membrane gas separation offers the advantage of avoiding solvents or liquid sorbents altogether, it often faces a tradeoff between permeability and selectivity, along with challenges like plasticization, thermal instability, and aging.

In contrast, this work employs a membrane contactor configuration. Rather than functioning as a selective separator, the membrane in this system serves as a physical interface—separating the gas phase (flue gas or ambient air) from the liquid sorbent while maximizing interfacial contact.

Here, CO₂ capture occurs in the liquid phase, and the membrane simply facilitates contact without participating in the chemical separation. This design enables the use of non-selective but chemically inert and robust membranes, such as expanded-polytetrafluoroethylene (EPTFE). The membrane separates the gas and liquid phases at the interface, providing the mass transfer contact area for CO₂ absorption and desorption. Compared to a conventional packed column amine process, a membrane contactor can provide greater mass transfer area per unit volume (1500–3000 m²/m³) compared to a column contactor (100–800 m²/m³) (61).

By using the membrane as a passive contactor rather than a selective barrier, this approach allows for integration of more chemically tunable liquid sorbents, potentially offering improved regeneration performance, scalability, and material longevity

1.4.1 Porous Membrane Materials

In membrane contactor configurations for CO₂ capture, the membrane serves as a physical barrier between the gas phase and the liquid sorbent, facilitating efficient mass transfer while preventing solvent leakage. Most membranes are inherently porous, and careful consideration must be given to the size and structure of these pores. Pores must be large enough to allow gas-phase diffusion to the sorbent interface, yet small enough to resist intrusion by the liquid sorbent.

If liquid penetrates and fills the pores—known as pore wetting—the CO₂ mass transfer rate decreases significantly, as diffusion through liquid-filled pores is several orders of magnitude slower than through open gas-filled pores (62) (63).

$$p_B = \frac{4\gamma\cos\theta}{d_{max}}$$

The susceptibility of a membrane to pore wetting is governed by the Young–Laplace equation, which relates the breakthrough pressure (i.e., the pressure at which the liquid enters the pores) to the surface tension (γ) of the solvent, the contact angle (θ) between the solvent and membrane surface, and the maximum pore diameter (d_{max}) (64). Membranes with high contact angles relative to the solvent exhibit greater resistance to pore wetting, as the solvent does not readily spread across or penetrate the surface—indicating hydrophobicity is a key desired trait. Materials such as polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), polyvinylidene fluoride (PVDF), are commonly used for this reason (65).

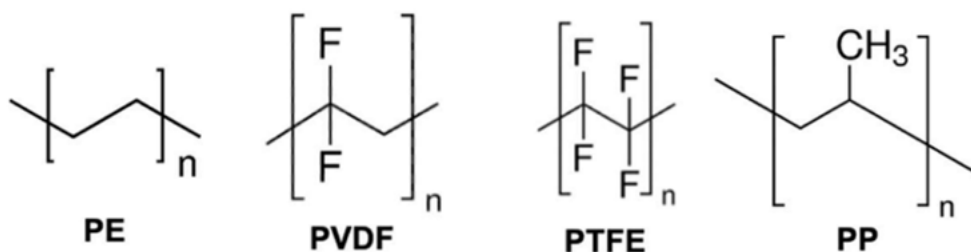


Figure 4 Chemical structure of membrane monomers

However, even initially hydrophobic materials can degrade over time. Amine solvents and their degradation products (e.g., formic, acetic, and oxalic acids) may gradually absorb into the membrane matrix, altering surface chemistry and reducing hydrophobicity (66). Therefore, membrane materials must not only be hydrophobic and resistant to pore wetting, but also chemically and thermally stable under operating conditions. Cost and manufacturability are also important, particularly for scalable systems. While polymeric membranes are popular due to their versatility and ease of fabrication, surface treatments and material modifications are often needed to preserve long-term performance in contactor systems but should be balanced with cost considerations.

1.4.2 Characterization Techniques of membranes

To ensure long-term functionality of membrane contactor systems in CO₂ capture applications, it is essential to evaluate both the initial physical structure of the membrane and its chemical and mechanical stability under operating conditions. Membranes exposed to reactive sorbents—such as amine-based solutions—and elevated temperatures can undergo physical degradation, chemical attack, or fouling, all of which impair performance. Several analytical techniques are commonly employed to monitor and characterize these changes over time.

Fourier Transform Infrared (FTIR) spectroscopy can be used to assess chemical modifications within the membrane or the surrounding sorbent solution. It enables detection of changes in functional groups on the membrane surface that may indicate oxidative degradation, hydrolysis

of polymer chains, or adsorption of solvent-derived byproducts. In addition, FTIR analysis of the liquid phase can help identify and track the formation of organic degradation products such as formic, acetic, or oxalic acid, which may contribute to fouling or alter membrane properties over time.

Nuclear Magnetic Resonance (NMR) spectroscopy is particularly valuable for identifying degradation products in the liquid phase with high specificity. Both ^1H and ^{13}C NMR can be used to detect small-molecule byproducts formed from amine degradation, including carbonates and low-molecular-weight organic acids. NMR allows for structural elucidation and quantification of these species, offering insight into degradation pathways and the chemical compatibility of the membrane with the capture solvent.

Scanning Electron Microscopy (SEM) is widely used to examine the physical morphology of membranes before and after exposure to capture conditions. SEM imaging provides detailed information on pore structure, size distribution, surface roughness, and the presence of any fouling layers or physical damage such as cracking, pore collapse, or delamination. Observing these changes can help correlate morphological degradation with performance losses, particularly in terms of gas diffusivity or sorbent interaction.

Contact angle measurements can also be used to assess changes in surface hydrophobicity, which is a critical factor in preventing pore wetting. A decrease in contact angle over time indicates an increase in wettability, often resulting from membrane oxidation, sorbent absorption, or surface contamination. This change directly affects the breakthrough pressure, as described by the

Young–Laplace equation, and may signal the onset of compromised performance in membrane contactor systems.

Together, these chemical and physical characterization techniques form a comprehensive toolkit for evaluating membrane degradation. They not only clarify the mechanisms by which membranes fail in reactive environments but also provide the data needed to optimize material selection and improve operational lifetime for CO₂ capture applications.

1.5 High Surface Area Contactors

The geometry of membranes used in membrane contactor systems plays a critical role in enhancing the efficiency of CO₂ uptake by increasing the interfacial area between the gas and liquid phases. This gas-liquid contacting step is a major contributor to the overall performance and cost of carbon capture systems, particularly in direct air capture (DAC) applications.

Techno-economic TEAs in literature have shown that the air-liquid contactor can represent more than 20% of the annualized capital costs of a DAC plant (67). This substantial cost is largely due to the physical scale required to enable sufficient contact between atmospheric CO₂ and the sorbent solution, making the contacting unit one of the most important components for process optimization.

In conventional air-liquid contactor systems, the capture solution is dispersed across high-surface-area materials—often fabricated from plastics such as polyvinylidene fluoride (PVDF), and occasionally reinforced with stainless steel elements for structural integrity. These contactor

materials are typically a few millimeters thick and are designed with intricate geometries to maximize the surface area available for gas-liquid interaction (67) (68). Air is forced over the wetted surfaces using fans, enabling CO₂ from ambient air to diffuse into the liquid phase and bind with the sorbent. The underlying principle is to maximize exposure of the sorbent to air, improving capture kinetics and reducing required contact time.

However, these high-surface-area systems introduce engineering challenges. Since large volumes of ambient air are flowed over volatile liquids—including aqueous solvents—significant evaporation can occur, leading to both solvent loss and energy penalties for solvent regeneration. Additionally, non-uniform distribution of the liquid sorbent over time due to gravity, clogging, or channeling can result in uneven contactor performance and reduced efficiency.

Hollow fiber membrane contactors (HFMCs) present a promising alternative to these traditional geometries. Like the high-surface-area contactors, HFMCs aim to maximize the interface between the capture solution and air but do so through a more controlled architecture. Instead of relying on gravity-driven dispersion over open surfaces, HFMCs consist of porous fibers fabricated from materials such as PVDF, PTFE, or other hydrophobic polymers. These fibers serve as both structural supports and selective barriers. Air or gas streams pass either through the fiber bores (lumen side) or over the shell side, while the liquid sorbent flows on the opposing side. This geometry enables consistent and scalable gas-liquid interaction within a compact, modular design.

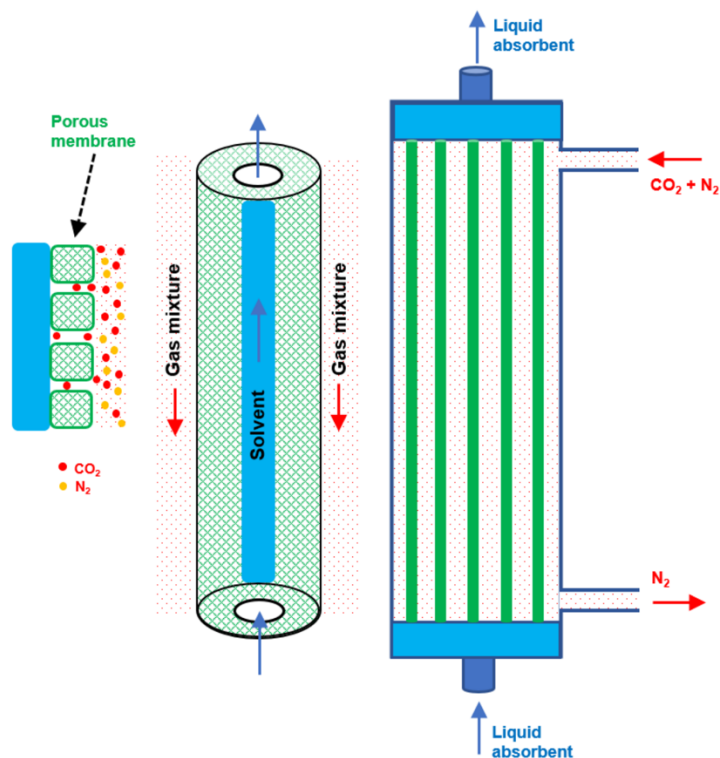


Figure 5 Functional diagram of a hollow-fiber membrane contactor (69)

In this work, the hollow fiber membrane contactor is leveraged as a stable interface that allows CO_2 to diffuse from the gas phase into the liquid sorbent with minimal pore wetting and solvent loss. The use of HFMCs aligns with the broader goal of enhancing gas-liquid mass transfer in a compact form factor, while minimizing the drawbacks associated with conventional air-liquid contacting systems.

2 Developing a Passive Photothermal System for Point-Source Capture

2.1 Introduction

While the photothermal release of CO₂ from capture solutions using NCBs has been demonstrated, no prototypes to implement this chemistry at scale have yet been developed. Current commercially available aqueous amine capture plants cannot satisfy the solar requirements for the photothermal release of CO₂, so retrofitting these systems has not been feasible.

This chapter focuses on the development of a passive photothermal system specifically for point-source CO₂ capture. While traditional systems rely on significant external energy inputs for solvent regeneration, this work explores whether ambient solar energy can be harnessed to passively regenerate amine-based solvents with minimal infrastructure. The goal of this device is to reduce energy costs and material complexity in real-world capture scenarios, such as industrial flue gas or remote facilities for DAC.

To achieve this, a laboratory-scale proof-of-concept device—termed the passive photothermal capture (PPC) system—was developed. Several design iterations were considered throughout the development of the device, and each iteration introduced new considerations that informed the final design. The system was ultimately developed to optimize the photothermal effect by optimizing the amount of photothermally active amine-solution exposed to solar irradiation while also optimizing the contact area for CO₂ absorption. The PPC enables a low regeneration temperature without sacrificing efficiency, using ambient sunlight instead of manufactured energy sources. The highest regeneration efficiency achieved with the device is 4.4 mol CO₂ per MJ, which is comparable to other established and commercial carbon capture methods.

2.2 Early Design Criteria and Proof-of-Concept Trials

The design of this system originated from a goal of leveraging the previously established photothermal chemistry to use sunlight to regenerate sorbent, while also enabling passively captured regenerated CO₂.

2.2.1 Glass Cylinder and PVC Membrane

A glass tube (50.8 mm H x 12.7 mm ID) was initially used as the housing for the capture fluid. This geometry was selected under the assumption that cylindrical symmetry would facilitate uniform light exposure from multiple angles. The tube was placed inside a reflective light tunnel lined with a highly reflective film (Ultra-Thin Reflective Mirrored Sheet, GreenPower Science) to maximize incident light. Illumination was provided by a high-intensity halogen lamp positioned outside the tunnel. The tube was filled with 5 mL of 30% MEA with 0.2 wt% NCBs. Polyvinyl chloride (PVC) membranes possessing pore sizes of approximately 45–65 nm and a thickness of 0.381 mm were epoxied to the ends of the glass tube. These membranes were affixed using epoxy and served as gas-permeable interfaces. One end of the system was connected via rubber tubing to a CO₂ sensor to monitor gas release.

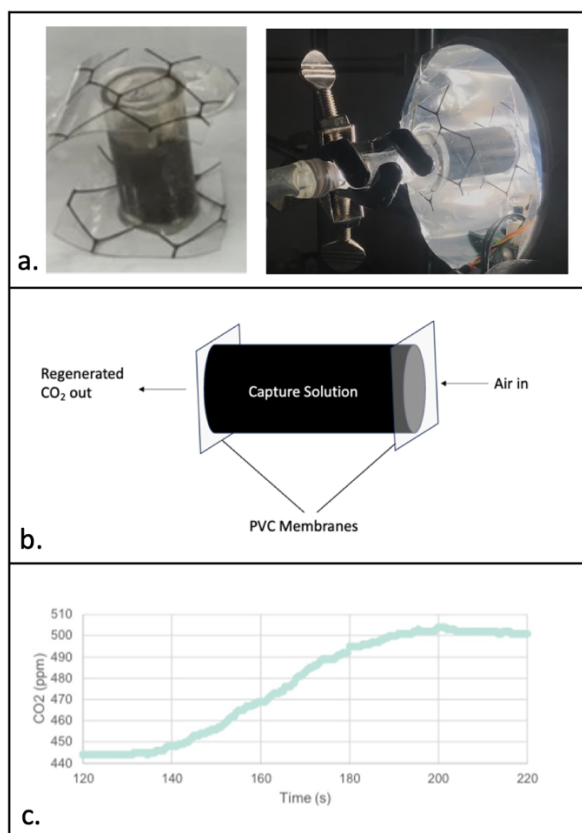


Figure 6 Starting-point design of capture system: a. Glass tube with PVC membranes, illuminated in reflective tube. b. Schematic of gas flow. c. Regenerated CO₂ at sensor

This first-generation device did achieve measurable CO₂ regeneration upon illumination, as indicated by a rise in CO₂ concentration when the lamp was activated. However, the overall performance was limited, with less than 60 ppm enrichment. Several design constraints contributed to its inefficiency. First, the pore size of the PVC membrane was likely too small to allow effective diffusion of CO₂, reducing the regeneration rate. Second, the system reached a maximum internal temperature of only ~60 °C, which was below the threshold required for efficient thermal desorption of CO₂ from the chosen sorbent. Additionally, ambient air was likely too optimistic as a feedstock for the system; higher concentration streams of CO₂ would be more suitable for this setup.

This initial setup provided a valuable starting point and it was subsequently modified to improve its performance as shown in Figure 2. The orientation was flipped and the lamp was pointed perpendicularly at the device to directly irradiate the device, increasing heat transfer to the sorbent. In addition, rather than relying on ambient air, the system was capped and supplied with a controlled CO₂ flow at 0.2 L/min. This created a slightly pressurized environment and ensured a consistent input concentration of CO₂ for capture. The CO₂-enriched air entered from the top through PVC membrane, passed through the capture sorbent, and was regenerated through thermal desorption induced by photothermal heating from a halogen lamp, and passed through the bottom PVC membrane. The effluent air was directed to a CO₂ sensor for real-time monitoring.

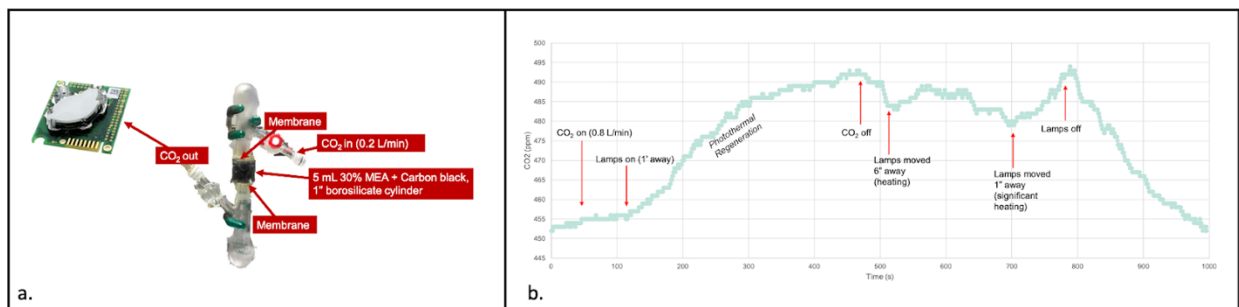


Figure 7 a. Design of vertical system using glass and PVC membrane with CO₂ input. b. Sample of output from system which describes experiment.

This iteration of the system produced consistent and repeatable CO₂ regeneration signals, representing a meaningful improvement over the previous design. The increased reliability of the output enabled more systematic testing of individual components and operating parameters. Three different membrane materials were tested in this improved prototype: 0.0625" expanded polytetrafluoroethylene (ePTFE), 0.012" polyvinyl chloride (PVC), and 0.005" cellulose. These

materials were selected based on their documented compatibility with aqueous amine solutions, a key requirement for sorbent contact. Additionally, the chosen membranes offered a range of pore sizes and thicknesses, which provided an initial basis for evaluating how material properties influence gas diffusion rates and overall system performance.

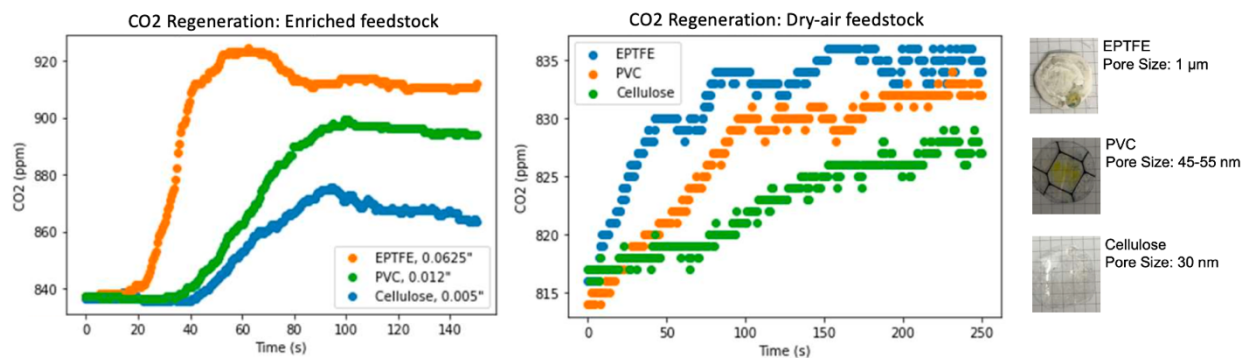


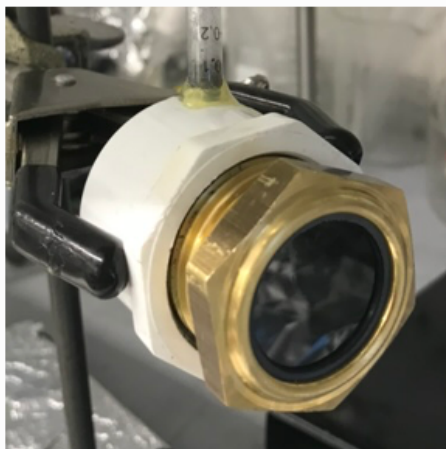
Figure 2-8 Impact of membrane material on CO₂ regeneration from enriched and dry-air feedstocks.

As expected, the ePTFE membrane yielded the highest efficiency in the system. This performance is likely attributed to its relatively large pore size, which facilitates faster CO₂ transport. The PVC membrane, with moderately smaller pores, exhibited intermediate performance, while the cellulose membrane, having the smallest pore size, resulted in the lowest efficiency. These results suggest that pore size, rather than membrane thickness, was the dominant factor influencing system performance. Based on these findings, ePTFE was selected as the membrane material for subsequent iterations of the device.

2.2.2 Threaded Device with EPTFE

After operating the previous device design for some time and gathering preliminary performance data, we identified several drawbacks that limited its usability and reproducibility. Chief among these was the challenge of reassembling the membrane between runs; each cycle required re-adhering the membrane, which was both time-consuming and inconsistent. Furthermore, epoxy seals frequently failed under heat, compromising the integrity of the system. To address these issues, we redesigned the device to incorporate more robust and thermally stable components while minimizing reliance on epoxy.

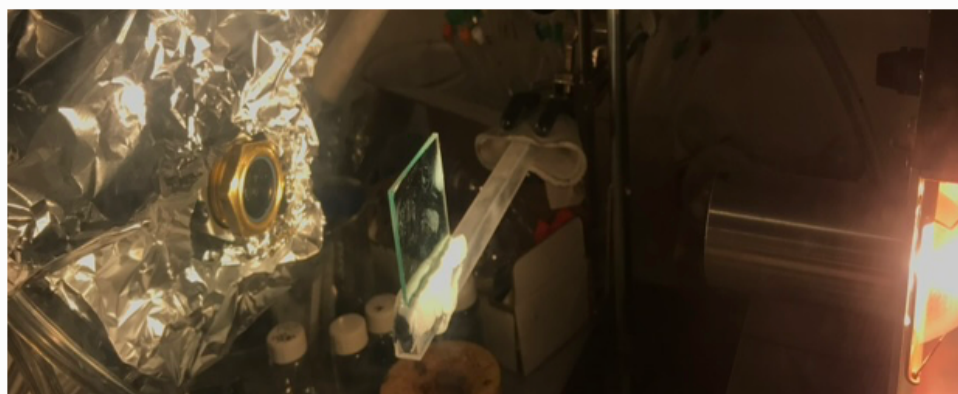
The new design featured a threaded brass sight glass with a 25 mm glass window at the front, allowing for both structural stability and light exposure. The back was constructed from a threaded PVC pipe cap with a 24 mm drilled opening. The ePTFE membrane was hot-glued over this opening, and a 4 mm hole was drilled at the top for CO₂ collection, also sealed with hot glue. This iteration prioritized physical seals over chemical adhesives, except in less critical areas. Hot glue replaced epoxy for sealing due to its improved ease of application and sufficient thermal tolerance—remaining stable up to approximately 79.4 °C, while the system operated near 70 °C. This configuration offered a higher surface area for both photothermal exposure and gas-sorbent interaction, both of which could still be further optimized in future iterations.



25 mm glass window



EPTFE Membrane



Experimental setup

Figure 9 Threaded Device with EPTFE Membrane and experiment setup

This apparatus performed significantly better than the previous iteration, due to several key improvements. First, the lamp was positioned directly in front of the prototype, allowing light to strike the flat glass window head-on. This eliminated the inefficiencies introduced by a curved surface in the earlier design and enhanced the thermal delivery to the sorbent. The performance of this prototype exceeded the detection limits of the CO₂ sensor in some cases, indicating strong regeneration.

We tested the device in a simulated flue gas environment containing 30% CO₂, which is representative of concentrations typically found in steel production exhaust. As shown in Figure 4, CO₂ regeneration clearly increased when the lamp was turned on and ceased when the lamp was turned off. Notably, the device was also able to regenerate CO₂ from more dilute streams; even at 2% CO₂, regeneration was observed.

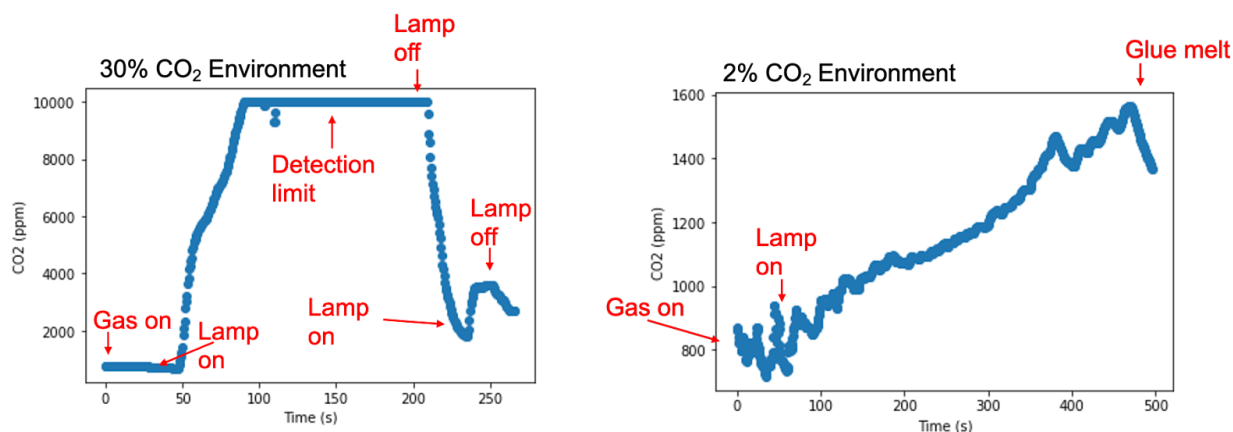


Figure 10 Performance of threaded device with EPTFE membrane

However, one limitation that emerged over time was melting of the hot glue used in certain seals. Prolonged exposure to heat led to failure at these points, which eventually reduced the regeneration efficiency. This observation highlighted the need for complete removal of thermal adhesives in future designs, and the incorporation of stronger physical seals.

2.2.3 Hermetically Sealed Device

Due to the efficiency loss caused by adhesive failure, we sought to develop a system that could be fully and hermetically sealed without the need for adhesives. This design choice offered an

added benefit: simplified setup and teardown. Rather than relying on bonding materials that could fail under heat, the components could be mechanically secured by tightening, improving both reliability and reproducibility.

After some investigation, we identified stock components that could accommodate a membrane and transparent window, with the sorbent solution enclosed between them. These components—stainless steel spools—were sourced from a supplier called Stout Tanks and Kettles. Though initially difficult to find, they turned out to be an excellent fit for our application. Notably, these materials are designed for use in beer brewing, a field that similarly requires durable, high-pressure sealing systems.

In this setup, the membrane could be held in place by sandwiching it between a ferrule with a rubber gasket and the steel spool body, secured tightly with a tri-clamp. The same manufacturer also offered acrylic windows that could be used as the light-facing surface. While the concept proved functional, the geometry of the available components posed some constraints. The initial prototype used a spool with a 3-inch radius and a 1-inch height. Ideally, a larger diameter and thinner profile would allow for increased membrane surface area and a more efficient, layered design.



Figure 11 Assembling the hermetically sealed device with EPTFE and stainless steel spools

2.2.3.1 Tyvek as a membrane

From our initial membrane comparisons—namely EPTFE, PVC, and cellulose—we observed that higher porosity generally correlated with improved device performance. Given that the new tri-clamp setup provided a strong and consistent seal, we hypothesized that it could also accommodate more flexible membrane materials that would have been difficult to work with using epoxy. This opened the door to testing ultra-thin, highly porous materials optimized for gas exchange.

The ideal membrane for this configuration needed to meet several criteria: (1) chemical resistance to aqueous amines, (2) hydrophobicity to prevent liquid breakthrough, and (3) large pore sizes to facilitate CO₂ diffusion. Based on these parameters, we identified Tyvek as a promising candidate. Tyvek is composed of spunbound polyethylene fibers and features pore sizes ranging from 0.002 to 100 microns—up to 100 times larger than those of EPTFE. It is approximately 0.2 mm thick and maintains a high-density, semi-solid structure that resists liquid penetration.

The device performed well when using Tyvek as the membrane material, allowing us to evaluate multiple components of the experimental setup. To simulate various CO₂ concentrations under non-pressurized conditions, the device was connected to an 'environment bag' affixed to the membrane side. The device was filled with 10 mL of capture solution composed of 30% MEA and 0.2 wt% NCBs. Prior to testing, the tubing was purged with N₂ and pumped down until the CO₂ output stabilized. The environment bag was then adjusted to the desired CO₂ concentration by introducing a controlled mixture of air and CO₂.

We tested the device under environments with varying CO₂ concentrations and initially positioned the heat lamp at a distance that delivered an incident power of approximately 1600 W/m² on the device window. Under these conditions, we observed the most effective CO₂ regeneration to date for our system.

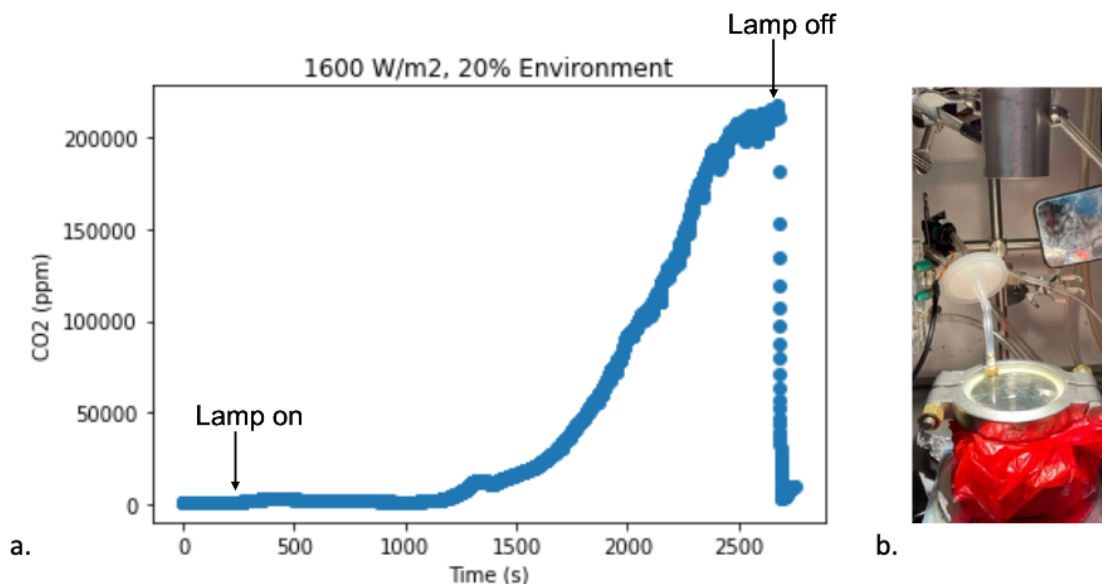


Figure 12 a. Regeneration of CO₂ in the hermetically sealed device using Tyvek in an environment enriched to 20% CO₂. b. Experiment setup where lamp is illuminating device

While Tyvek initially performed well under test conditions, it demonstrated degradation over time and inconsistent behavior under sustained exposure, limiting its long-term reliability in this application. The material would leak capture solution, and would develop holes overtime. We subsequently returned to using EPTFE in the system.

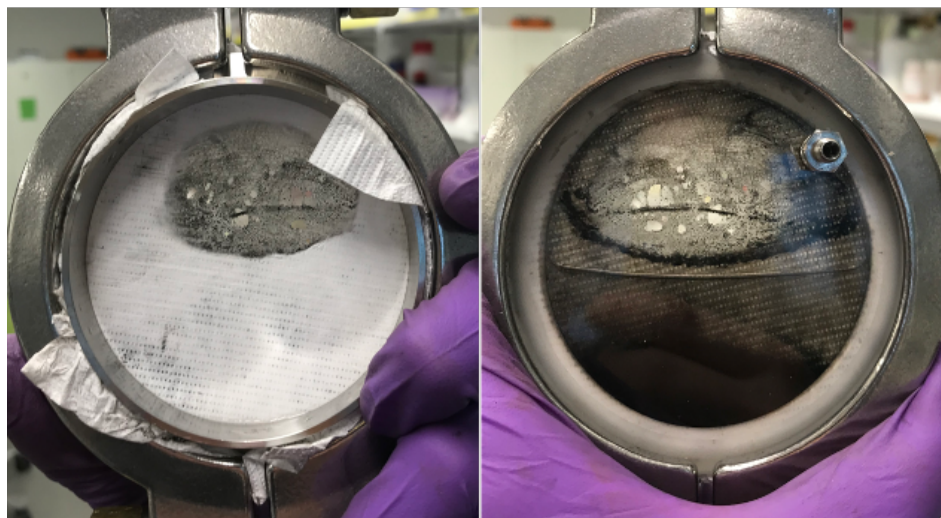


Figure 13 Example of the degradation of Tyvek after repeated use

2.2.3.2 Headspace-free Configuration

In returning to ePTFE as a membrane, we wanted to minimize the headspace within the device. Ideally, a minimal headspace would reduce the volume of non-reactive air relative to the 1–10 mL of capture solution used, thereby improving the accuracy of CO₂ measurement. However, headspace also serves a critical function: it provides a region for CO₂ to accumulate efficiently after being photothermally released from the solution. We aimed to determine the smallest possible headspace that would still allow for effective CO₂ release and system operation.

Our initial approach to minimizing headspace involved removing the stainless steel spool and instead sandwiching the capture solution between the membrane and the window, separated only by a ~1 mm rubber gasket. This design had theoretical advantages: despite using only 1 mL of solution, it allowed full contact with the membrane, maximizing the surface area-to-volume ratio and potentially enhancing gas diffusion. However, this configuration ultimately proved unworkable—some degree of headspace is necessary.

The lack of headspace introduced several issues. First, it appeared to hinder CO₂ release, likely due to gas build-up or limited diffusion pathways. In some cases, CO₂ regeneration would abruptly stop and fluid would back up into the outlet port, making continuous operation difficult. This behavior is evident in Figure 8d, where a sudden halt in CO₂ release is followed by a sharp spike, suggesting periodic blockages and pressure release events.

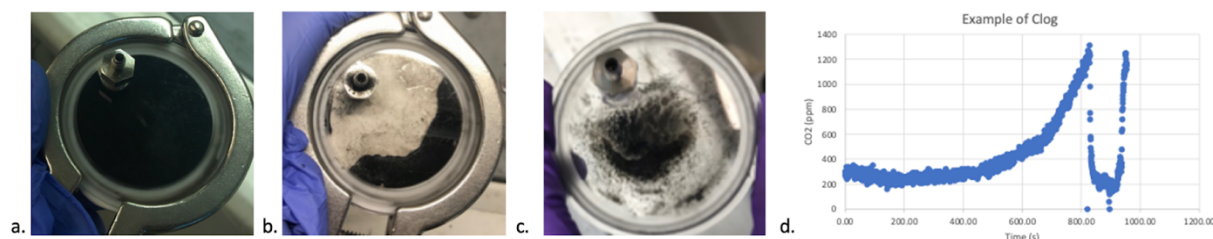


Figure 14 Design challenges with a headspace-free configuration. a. Device prior to operation, filled with capture solution. b. After operation, carbon black visibly separates from the solution c. Deposition of carbon black on the acrylic window, reducing light transmission. d. Graph showing CO₂ release rate over time, illustrating a clog event.

Additionally, carbon black began to separate from the solution and accumulated along the perimeter of the device, as shown in Figure 8b. This separation may be due to chemical incompatibility between the capture solution and the acrylic window, leading to aggregation over

time. After multiple runs, the window became heavily stained with carbon black, further suggesting a materials interface issue.

2.2.3.2 Initial Solvent Tests

Over time, we observed that the capture solution became increasingly viscous during operation, likely due to continuous heating and the gradual evaporation of water. Despite this change, the system continued to regenerate CO_2 , which prompted us to question whether the solution truly required the typical 30% MEA (monoethanolamine) concentration cited in literature. To test this, we ran the system under a 15% CO_2 environment with varying MEA concentrations. These tests confirmed that regeneration was most effective at or near 30% MEA in water, aligning with established findings.

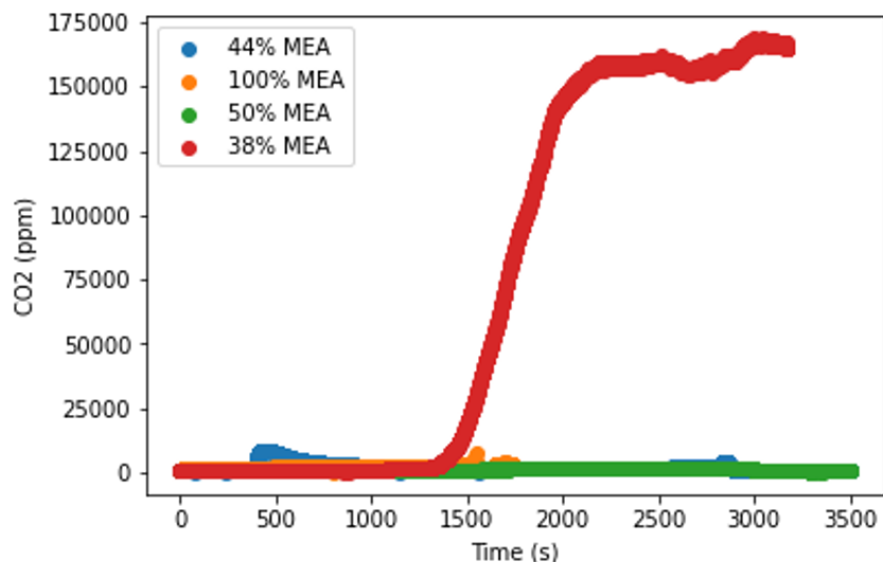


Figure 15 Effect of MEA concentration on CO_2 regeneration.

We also investigated the compatibility of the system with various co-solvents, since previous research has shown that co-solvents can enhance the photothermal regeneration performance of aqueous amines. One study evaluated total regeneration efficiency and maximum CO₂ release rate using a 1:1 co-solvent-to-water ratio with MEA (70). From that study, DMF (dimethylformamide), DMAC (dimethylacetamide), and methanol emerged as promising candidates due to their favorable boiling points, low viscosities, high regeneration efficiencies, and chemical compatibility with EPTFE membranes.

Cosolvent	Boiling Point (°C)	Viscosity (cP)	Regeneration Efficiency (mol/MJ)	Maximum CO ₂ Release Rate (g/h)
DMF	152	0.9	5.57 ± 0.36	1.41 ± 0.07
DMAC	165	0.9	4.82 ± 0.42	1.34 ± 0.11
MeOH	65	0.5	1.7 ± 0.19	2.70 ± 0.14

Table 2 Cosolvent properties with Photothermal Regeneration (70).

We initially tested the compatibility of potential co-solvents with the EPTFE membrane using a simple wetting test. Methanol was immediately ruled out, as it fully penetrated and wetted the membrane within seconds—making it unsuitable for the system, since solvent would readily seep through. DMF also showed some degree of wetting, though less severe. In contrast, DMAC demonstrated minimal wetting behavior and maintained a high contact angle on the membrane surface, indicating lower permeability and better compatibility. This initial test suggested that DMAC was far more suitable for use with EPTFE in a sealed system.

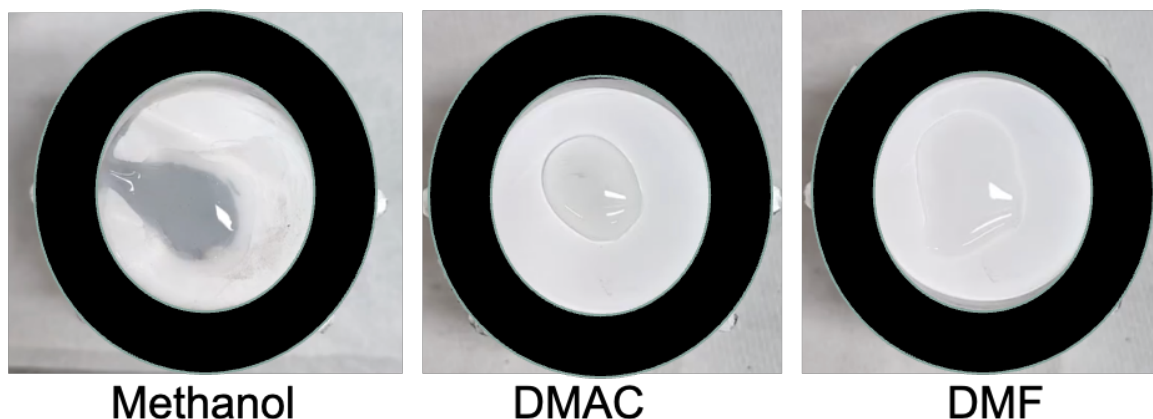


Figure 16 Wetting test of different sorbents on EPTFE membrane

We compared the system's CO₂ output using DMF and DMAC as co-solvents under controlled conditions. The experiment used a 15 mL solution containing 30% MEA with a 1:1 solvent-to-water ratio, exposed to 2500 W/m² of light in environments containing either 15% or 10% CO₂.

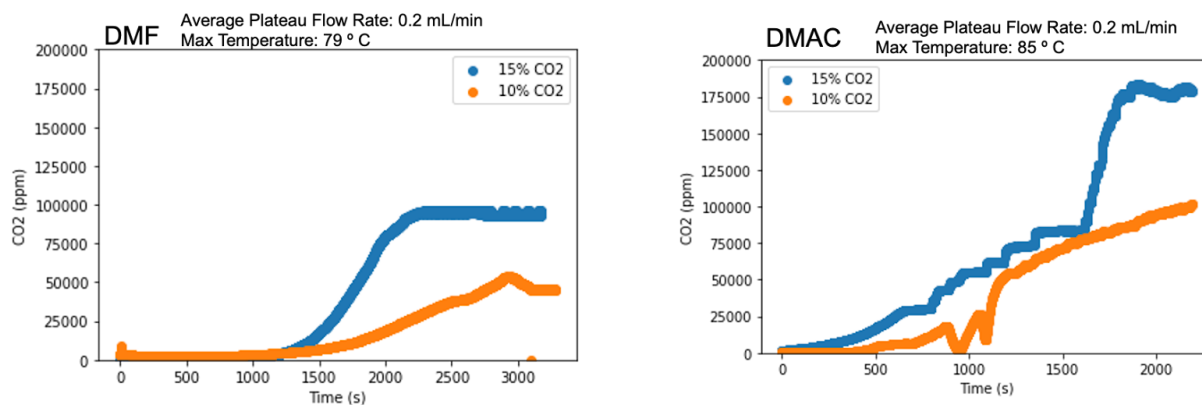


Figure 17 Experiments using DMF and DMAC as cosolvents to water.

Although DMF is known for its favorable regeneration efficiency, our tests showed that DMAC consistently produced higher overall CO₂ output. This was likely due to its ability to reach higher operational temperatures, which is critical for photothermal regeneration. Additionally, DMAC

exhibited better compatibility with the EPTFE membrane over time—while DMF tended to soften or swell the membrane with repeated use, DMAC maintained membrane integrity and seal quality more reliably. Considering both the superior regeneration performance under practical conditions and the improved membrane stability, we chose DMAC as the co-solvent for subsequent experiments.

2.3 Working Prototype of PPC Device

After extensive iteration with different geometries, materials, capture solutions, and solvents, the prototype reached a stable, repeatable configuration suitable for systematic testing. This section outlines the final design of the device and presents its performance characteristics.

The PPC device outlined in Figure 1 uses the general design elements composed of: (1) a window, to allow light to enter and heat the capture fluid; (2) a capture solution chamber, where CO₂ is bound and regenerated with a small headspace between the window and capture fluid; (3) a hydrophobic porous membrane, serving as a gas-liquid contactor for CO₂ uptake.

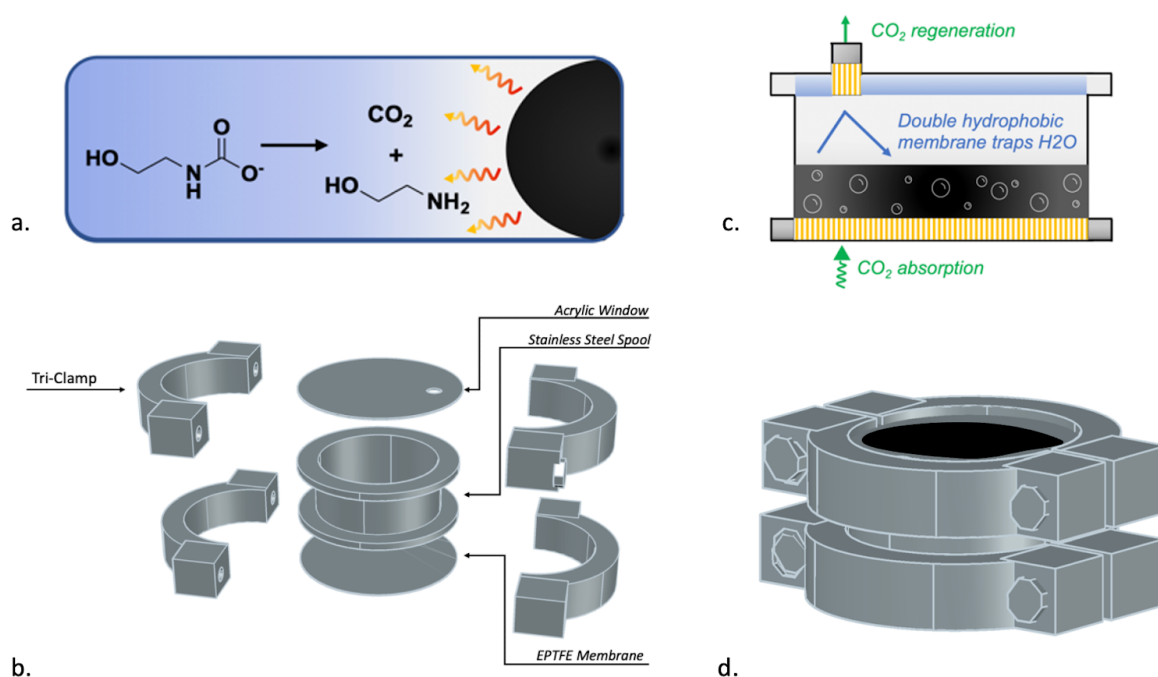


Figure 18 Device components include a stainless steel spool and tri-clamps which house the nano-solution. An acrylic window allows light to pass into the sample while the EPTFE membrane allows gas to flow through.

2.3.1 Window for PPC Device

The window material was selected for a combination of transparency and ease of fabrication. An acrylic (PMMA) window (Stout Tanks and Kettles) was selected because it had a similar index of refraction to glass (Glass = 1.52, Acrylic = 1.449). Additionally, acrylic can be easily modified with outlet ports while glass would require special equipment. The acrylic window has a maximum operable temperature of 80C, so it needed to be replaced frequently to prevent fogging and warping. The device was sealed hermetically with a stainless steel spool and tri-clamps as shown in Figure 18 (Stout Tanks and Kettles).

2.3.2 Membrane Preparation of PPC Device

The membrane was selected based on the CO₂ transport, stiffness, and limitations in fouling capabilities. The membrane is an EPTFE sheet material (USA sealing Inc.) with 0.39 mm thickness cut into 75 mm diameter circles. EPTFE was chosen as the membrane material because it is an inert material that exhibits hydrophobic surface properties due to its fluorinated backbone. These qualities prevent the material from breaking down while in contact with the corrosive amines and other solvents used in this system. Other membrane materials were considered—including Tyvek with 0.15 mm thickness and EPTFE with 0.8 mm thickness. While Tyvek was thinner than the chosen EPTFE, which would facilitate faster gas-diffusion, it could not withstand repeated use without tearing. The selected EPTFE strikes a balance between being thin enough for gas exchange, and robust enough for continuous and repeated use. EPTFE does have some drawbacks, however. Due to the hydrophobic nature of EPTFE, prolonged exposure to the aqueous amine solution caused membrane wetting and subsequent loss of CO₂ absorption. These drawbacks required that the membrane material be replaced regularly between runs.

2.3.3 Preparation of Amine Nanosolution

The capture solution was chosen based on compatibility with the device and previous experiments showing the capture and release capacity of photo-thermal fluids. The capture fluid used in the device was composed of 30 wt% MEA (monoethanolamine), 35 wt% DMAC (n,n-dimethylacetamide), 25 wt% water. A nanosolution was prepared by dispersing 0.2 wt% oxidized NCBs via ultrasonication for 20 minutes. DMAC was selected as a cosolvent to water

because it was found to improve the regeneration of CO₂ captured by MEA and has a relatively high boiling point compared to water. Other cosolvents, such as methanol and DMF, were also considered. However, methanol was incompatible because EPTFE could not prevent low surface tension liquids from wicking. Additionally, DMF deteriorated the device membrane and window. Due to these incompatibilities with device components, they were not selected. The device was operated using 11 mL of capture fluid stirred at 140 RPM with a stir bar.

2.4 Experimental Design

The PPC device has been designed to be implemented as a point-source capture or eventually a potential direct air capture (DAC) method in the future. CO₂ concentrations typically found in industrial flue gas and ambient air range from 8-33% as shown in Table 3. To simulate these CO₂ concentrations, the membrane-side of the device was connected to a non-pressurized chamber which was filled with a ratio of air and CO₂. The concentration of CO₂ in the simulated environment was recorded with an IR CO₂ sensor (Gas Sensing Solutions, SPRINTIR-W-F-100). As outlined in Figure 3, a halogen lamp was placed 14 cm above and directed at the window of the device. This distance was selected because it applies an average illuminance of 1250 W/m² on the device, which is similar to what the device would experience via solar irradiation. Trials were performed to gauge the efficiency of the device in different industrial flue-gas contexts. Experiments were run in sets of 2.

Table 3 Typical CO₂ Enrichment in industrial gas streams (71)

Gas Source	CO ₂ Enrichment
Cement Manufacturing (Flue Gas)	25-33%
Coal (Flue Gas)	12-15%
Natural Gas Processing (Flue Gas)	8-10%
Tailpipe Emissions (Exhaust)	14-16%
Ambient	~0.04%

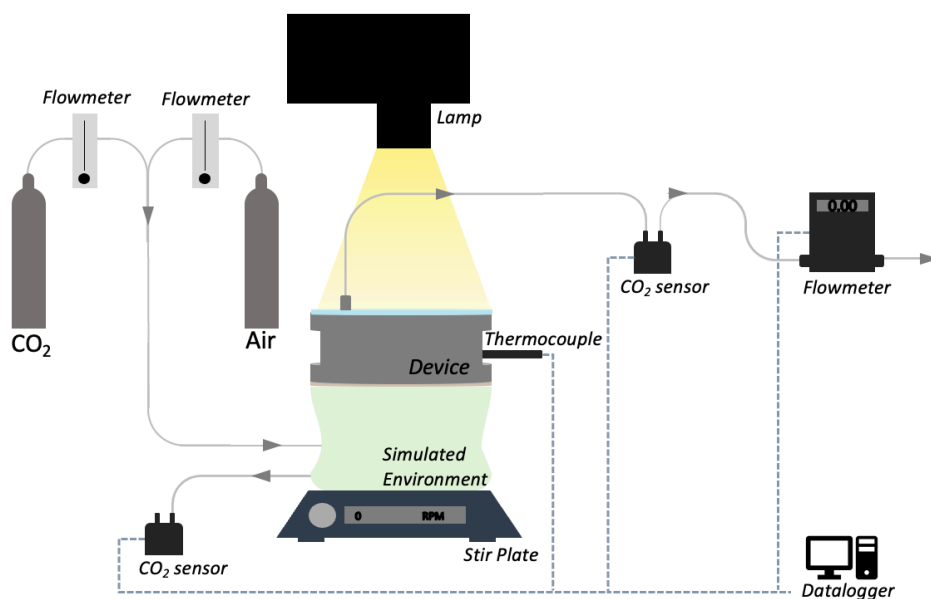


Figure 19 Experimental setup for lab-based tests. The environment chamber is filled with a preset ratio of air and CO₂, which passes through the device and is regenerated via lamp.

2.4.1 Efficiency analysis

Efficiency was calculated as a function of energy absorbed by the capture solution through the device window. We measured irradiance with an illuminance meter (Extech) which was averaged over the surface area of the window. We computed the average light intensity to be 1250 W/m² when the lamp was placed 14 cm away. Efficiency was computed within the region at which CO₂ output begins to plateau as indicated in Figure 20. Integrating under this plateau region gives the total number of moles of CO₂ regenerated for a given period of time. This was then divided by the total amount of energy used (MJ) to run the system for that period of time.

$$Irradiance \left(\frac{W}{m^2} \right) * time(h) * surface\ area\ of\ window\ (m^2) = Power(Wh)$$

$$1\ Wh = 0.0036\ MJ$$

$$Efficiency = \frac{Regenerated\ CO_2\ (mol)}{Power\ (MJ)}$$

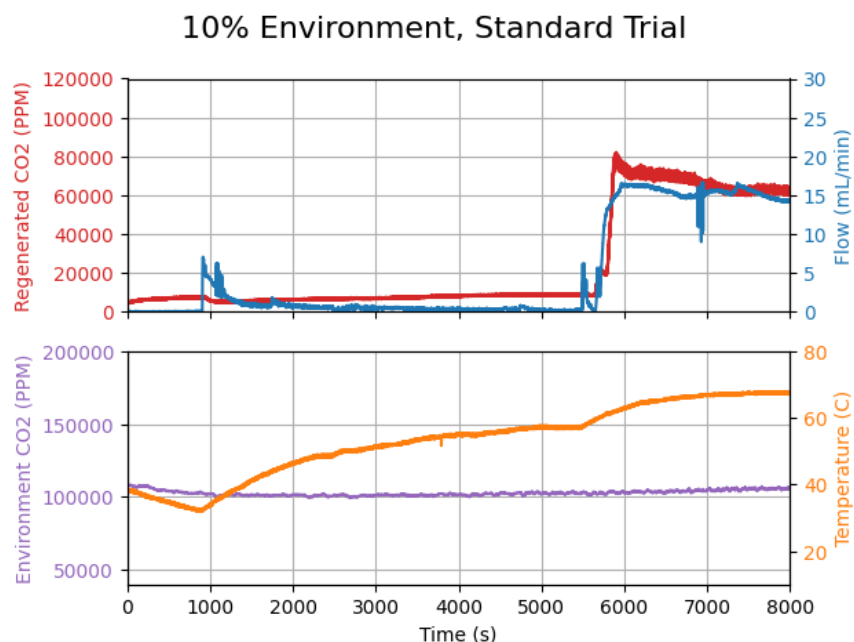


Figure 20 Results from a standard run in an an environment of 10% CO₂. There is an initial flow-peak at 1000s which is the time the lamp was turned on in this case. Regeneration occurs at 5000 seconds. The rate of CO₂ regeneration plateaus when the system reaches

2.5 Performance of PPC Device

2.5.1 Concept Verification

To demonstrate how the PPC device could be implemented as a point-source capture system with sunlight as an energy source, we conducted experiments in environments with varying levels of CO₂. As an initial test, we found that the device requires a “loading period” – time for the device to absorb CO₂ from the environment to achieve saturation while the lamp is turned off.

Assuming the capture fluid is saturated at 0.5 mol CO₂/mol MEA, we calculated that the solution will reach maximum loading at 4 g CO₂, which correlates to ~17 minutes of loading. From these assumptions, we selected a loading period time of 20 minutes as a baseline for testing the device

to ensure maximum CO₂ saturation of the capture fluid (supplementary material). At the end of the loading period, the lamp is turned on and the capture fluid begins the photothermal regeneration process. The gas stream flowing out of the device when the lamp was turned on passes through drying tubes (Nafion) to remove water vapor.

To measure regenerated CO₂, the output of the device flowed through the IR CO₂ sensor and a digital flowmeter (Aalborg). Concentration and flow rate were used to calculate the release rate of CO₂. A standard run of the device is shown in Figure 20 which illustrates how CO₂ regenerates and how temperature changes as a function of time. An initial spike in flowrate is seen immediately after the lamp is turned on as indicated in Figure 20. We attribute this spike in flowrate to the sudden expansion of gas in the device due to the lamp's added heat. This initial spike in flowrate diminishes within 10 minutes as the solution increases in temperature from light exposure from the lamp. It takes approximately one hour for the solution to reach its regeneration temperature. As the solution reaches 70°C, the release of regenerated CO₂ at the bulk scale is observed. This regeneration point is marked by a second peak in flowrate as shown in Figure 20 and increase in the mixing ratio of CO₂, which represents the system reaching its steady state.

The photothermal effect initiated by the NCBs is a key component in the design of the PPC device. A control trial was conducted which utilized the capture solution without NCBs to validate the role of NCBs. The results of the trial, as shown in Figure 21, demonstrate how the system does not regenerate CO₂ in the absence of NCBs. Although the temperature of the capture fluid surpasses the temperature required for photothermal regeneration, there is no

increase in CO₂ output. This confirms that, in a mild temperature regime (70 to 120 C), the photothermal effect provided by the addition of NCBs is responsible for CO₂ regeneration by our device. This result confirms that the device depends on the presence of NCBs to initiate photothermal regeneration.

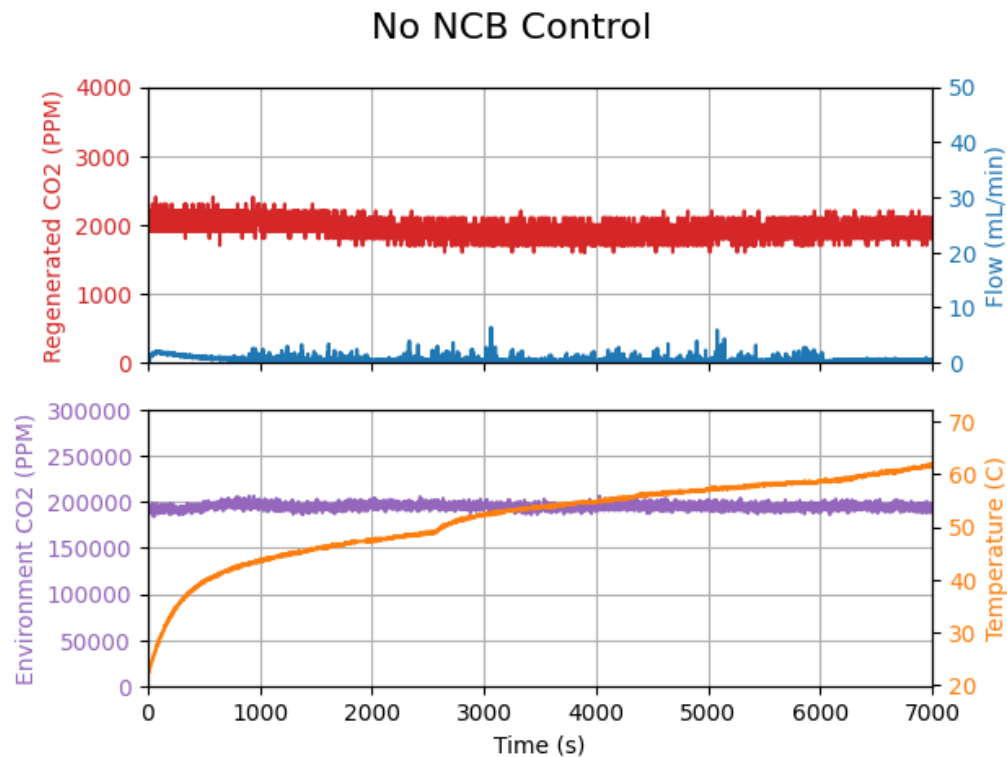


Figure 21 Control run without NCBs

2.5.2 Impact of Environmental Saturations of CO₂

The typical CO₂ concentration of a resulting flue gas stream varies for different industrial processes. As shown in Table 3, the standard range of industrial processes produce CO₂ in concentrations between 8-33% (Metz et al., 2005; Husebye et al., 2012; Liguori and Wilcox,

2018). To gauge the potential of our device for industrial use, we ran the device in environmental saturations of CO₂ within this range.

We sought to determine what ranges were optimal for device operation. As shown in Figure 22, the device regenerates more CO₂ when implemented in environmental concentrations of high CO₂ than it does in environments with low concentrations of CO₂. This result is not surprising given MEA's known chemistry. Additionally, the onset of regeneration of CO₂ is faster in higher concentrations of CO₂—such as 20%, than the lower ranges. An environment saturated to 20% (200K ppm) CO₂ results in the highest device output. At its maximum, it regenerates 1.8×10^{-6} moles of CO₂ per second and has the most pronounced drop to reach steady-state. An environment saturated to 5% (50K ppm CO₂) results in the lowest device output. At its maximum, it regenerates 0.09×10^{-6} moles of CO₂ per second and does not drop to reach steady-state. Each concentration reaches a different equilibrium output mixing ratio once steady state is achieved.

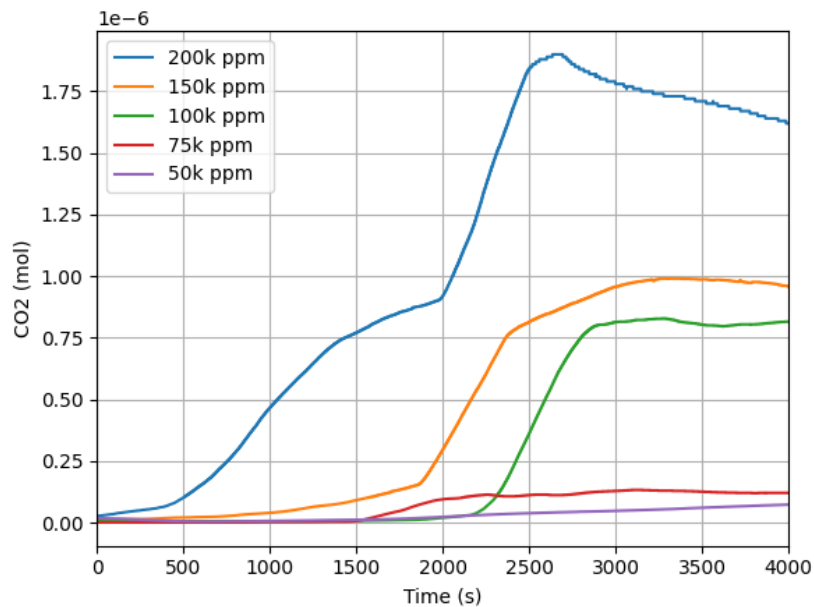


Figure 22 Output of CO₂ in moles for variation in environments containing different concentrations of CO₂.

Given the range of absorbance capacities, we wanted to determine what led to the highest efficiencies in the ability to absorb and release CO₂. The computed efficiencies in Figure 23 directly reflect the moles of CO₂ regenerated from each environmental saturation regime. As expected from the regeneration plots in 6, it is evident that higher environmental saturations of CO₂ result in higher efficiencies of the device. This result can be applied to a device's potential industrial use cases. If used downstream of a cement or coal plant, the device would run more efficiently compared to a natural gas processing plant. However, because the device can be powered using sunlight as an energy source which is cheaper than traditional manufactured energy sources, these efficiencies should primarily be used as a metric for future improvements.

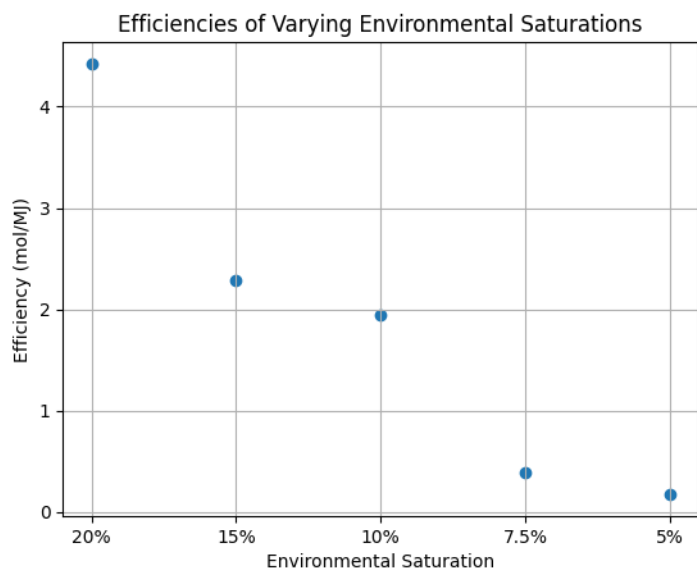


Figure 23 Effect of environmental saturation of CO_2 on device efficiencies.

The device did not regenerate CO_2 in an environmental saturation regime reflecting ambient air which is 0.04-0.1% (400-1000 ppm). One possible explanation of the lack of uptake at very low concentrations is the balance between the rate at which CO_2 is taken up through the membrane and into the solution and the rate of release. The solution may not be able to achieve sufficient levels of CO_2 from ambient air conditions, which is up to 3 orders of magnitude lower than the concentrations found in industrial flue gas. Put simply, the rate of release with the lamp on is much greater than the rate of uptake in ambient air conditions - thus driving the equilibrium in the wrong direction. This balance is illustrated in Figure 24. What is certain is that currently, this device is unable to regenerate statistically significant amounts of CO_2 from ambient air concentrations of CO_2 .

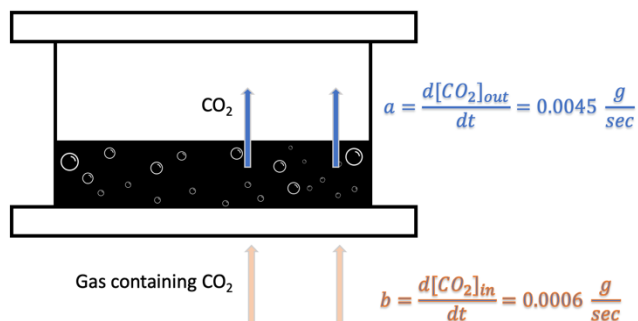


Figure 24 The flow of CO₂ within the device is balanced between the input rate and output rate

2.5.3 Light Cycling

The irradiance of sunlight at ground-level is not constant due to the presence of clouds and day to night variations, and in previous runs the device was operated under a constant light source. To test how this system responds to variations in illuminance, we ran two trials of varied cycle length. One covered an hourly cycle, mimicking large weather patterns, while the other covered a shorter 10 minute cycle, mimicking small cloud coverage on a partly cloudy day.

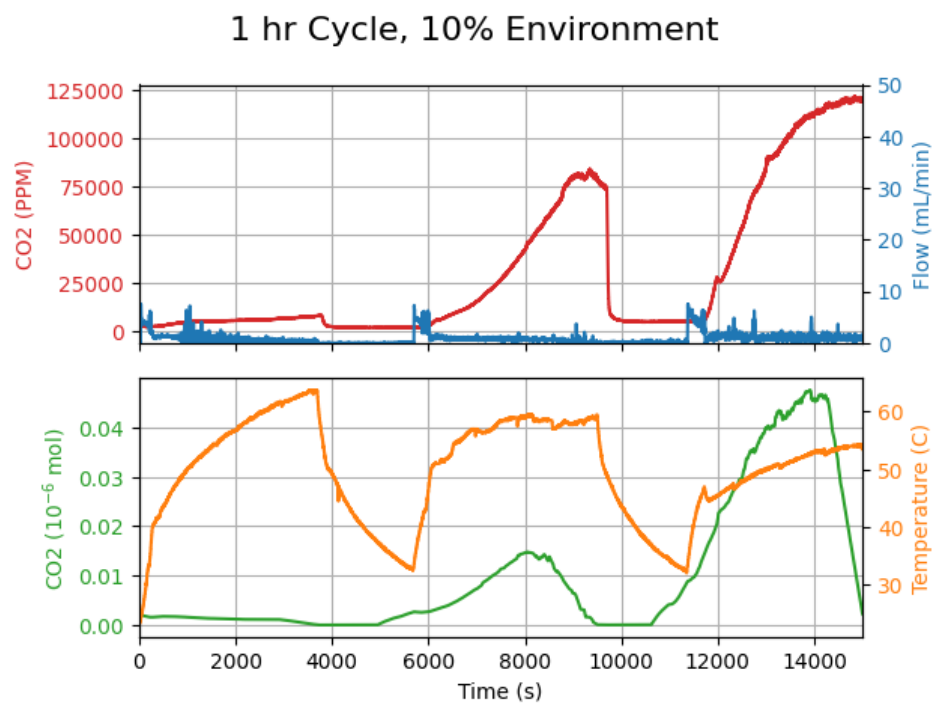


Figure 25 Output of CO₂ while being light-cycled for hour-long periods

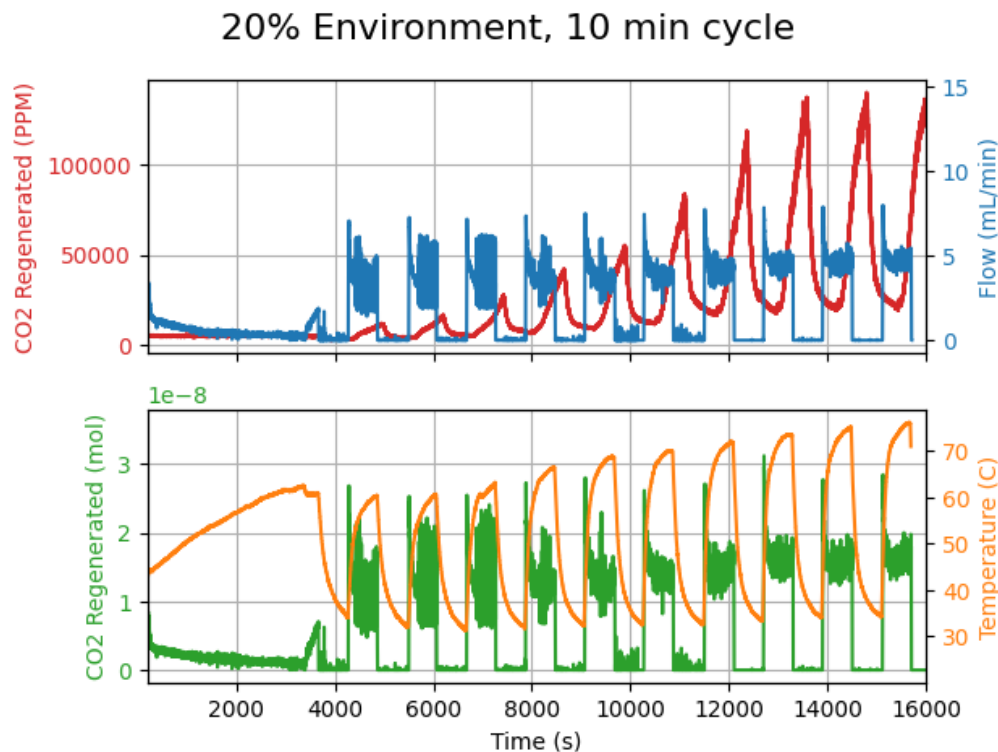


Figure 26 Output of CO₂ while being light-cycled for 10 minute periods.

The results of the 1 hour cycling process and 10 minute cycling process are shown in Figure 25 and Figure 26. Both processes effectively regenerated CO₂ in an environment saturated to 20% CO₂. However, the device regenerates more CO₂ when cycling every 10 minutes. This is likely due to the time-balance outlined in Figure 24. During the longer cycling process, the capture fluid reaches its maximum concentration of CO₂ during the 1 hour loading period. Once the lamp is turned back on, the absorbed CO₂ is released in a shorter period of time than it took to load the solution. The device is limited by how quickly CO₂ is absorbed into solution. We have approximated rate of absorption through the EPTFE membrane to be 0.0006 g/sec and the rate of release to be 0.0045 g/sec. The mass can be described by the following equation:

$$c(t) = CO_2 \text{ concentration}$$

$$C(0) = 4.2g$$

$$R = 0.0006 \text{ g/sec(rate in)}$$

$$r = 0.0045 \text{ g/sec(rate out)}$$

$$c(t + \Delta t) = c(t) + (R - r)\Delta t$$

$$dC/dt = (R - r)$$

$$c(t) = C(0) + (R - r)t$$

$$c(t) = 4.2g + (0.0006 - 0.0045)t$$

$$t = 18 \text{ mins}$$

The light-cycling experiments helped us to understand how cloud coverage and other weather patterns might impact the device's efficiency. However, these results might suggest new ways to apply the device. The device is limited by the rate of uptake through the porous membrane and into solution. By giving the device discrete and frequent breaks from light to cool and reenter the CO₂ absorption state, the device performs more efficiently. The potential explanation for this phenomenon is that the capture solution is more readily saturating with CO₂ and quickly releasing it.

2.5.4 Outdoor Performance

To test how the device would work using sunlight instead of a lamp, we ran trials of the device during sunny days in the summer and early fall. As shown in Figure 27, the device was set up similarly to lab-based runs, but used a standard enrichment of 15% CO₂ and used sunlight instead of a lamp. To simulate flue gas, the device was placed in a non-pressurized bag which was continuously pumped with 15% CO₂. A 200x200 mm Fresnel Lens (Six Seasons) with a 210 mm focal length was directed at the device and manually moved throughout the run to follow the path of the sun. A solar power meter (TES) recorded the baseline irradiance. The Fresnel Lens amplified the baseline irradiance by a factor of 2.

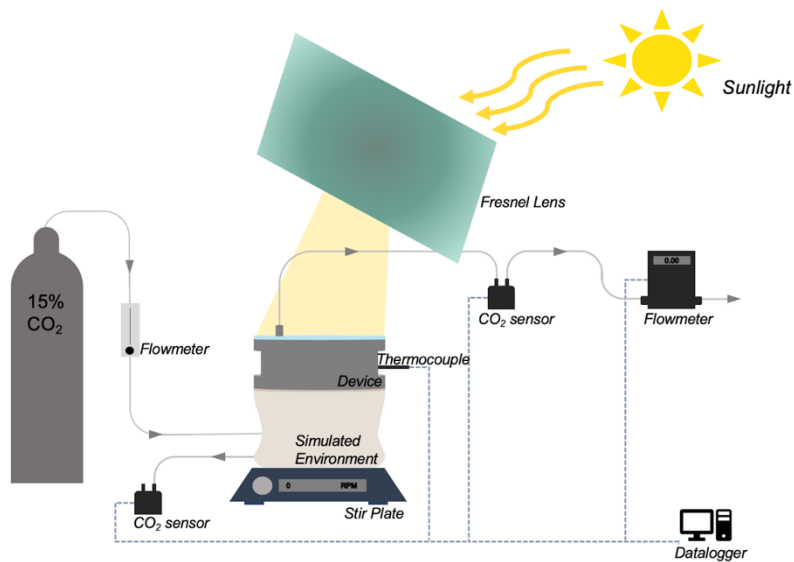


Figure 27 Experimental setup for outdoor-based tests. The environment bag is filled with a preset ratio of air and CO₂, which passes through the device and is regenerated via sunlight which passes through a fresnel lens.

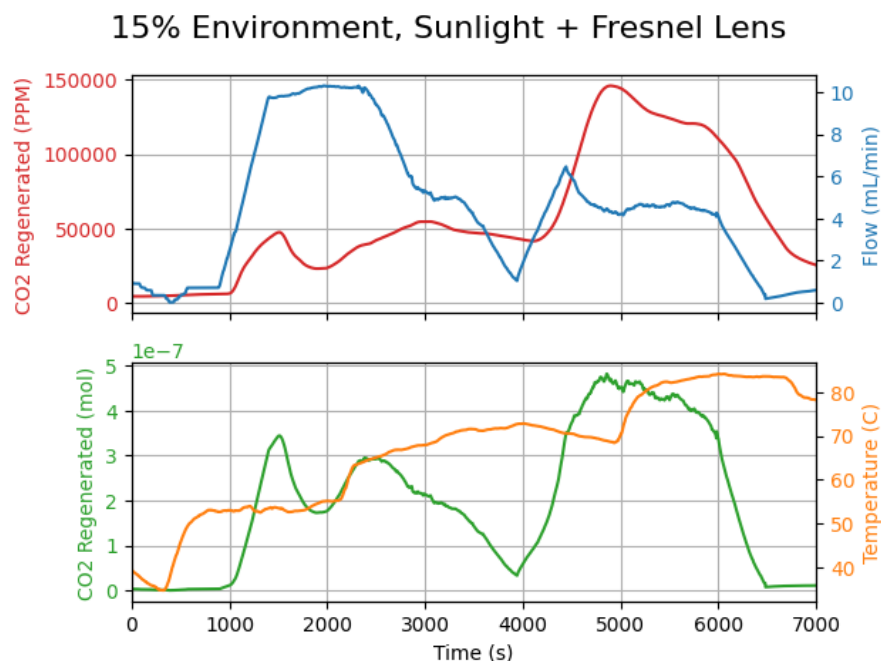


Figure 28 Output of CO₂ while being run continuously outdoors

The results of the outdoor run on October 2, 2023 from 12 PM - 3 PM, are shown in Figure 28.

This day was particularly sunny with limited cloud coverage. The illuminance meter recorded the irradiance as 760 W/m². The Fresnel lens effectively heated the capture fluid to a maximum temperature of 78°C. While this temperature is well beyond the minimum regeneration point for the capture fluid, the experiment showed that ambient solar light when concentrated by 2X can be used to heat the solution to its minimum temperature required for regeneration with carbon black nanoparticles. The device worked effectively in this environment. However, the efficiency of the device was lower in this setup than in a lamp-based setup.

2.6 TEA of PPC Device

A key motivation behind developing the PPC device was to tackle the scalability challenges that hinder many carbon capture systems. Scaling these technologies often presents significant obstacles, with cost being one of the most pressing concerns. Many carbon capture methods become prohibitively expensive due to their reliance on complex chemical processes that are difficult to synthesize and maintain or because they require substantial energy inputs to function effectively. While the PPC device demonstrated only modest performance compared to some other carbon capture approaches, it offered a crucial advantage: the ability to scale without imposing an additional energy burden on renewable sources, as it could operate solely on sunlight. To evaluate the feasibility of scaling the PPC system, we conducted a techno-economic analysis (TEA) to estimate the costs associated with expanding the device from a bench-scale 10 mL system to a version capable of capturing one ton of CO₂.

To conduct this analysis, we incorporated several key assumptions. One assumption was that approximately 10% of the solvent would evaporate over time. Additionally, we assumed that the output gas would undergo drying and compression for pipeline transport to underground CO₂ storage. Ideally, this process requires pressures exceeding 1,200 psi, which, based on our findings, requires the use of a 5,000 HP centrifugal compressor consuming approximately 90 kWh per day. It is important to note that different CO₂ transport methods—such as rail, trucking, or direct-to-storage—demand varying levels of compression, while certain CO₂ utilization pathways may not require compression at all.

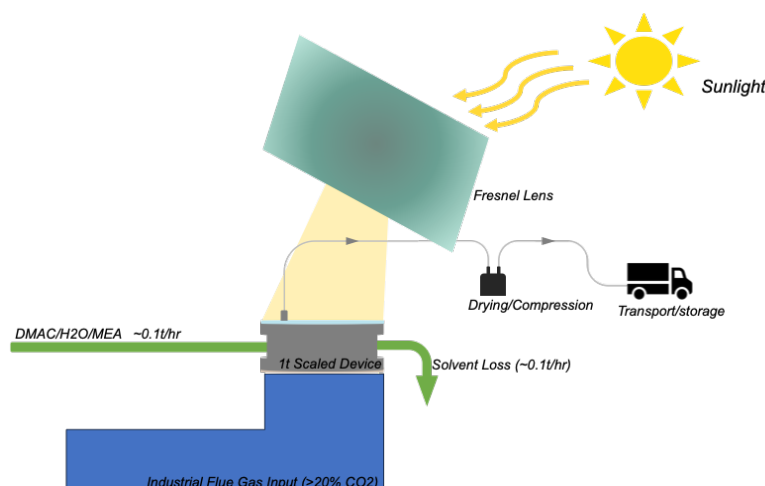


Figure 29 Schematic of scaled model for TEA

Cost considerations for the PPC device can be categorized into capital expenditures (CAPEX) and operating expenditures (OPEX), each of which can be further subdivided. Within CAPEX, costs are divided into Inside Battery Limits (ISBL) and Outside Battery Limits (OSBL). ISBL encompasses all essential process units, equipment, and infrastructure directly involved in production, such as reactors, distillation columns, pumps, and compressors. OSBL, on the other hand, refers to supporting infrastructure located outside the plant's immediate operational boundary, including utility systems such as water treatment facilities, power generation units, storage tanks, and loading stations.

To estimate OSBL and ISBL costs, certain standard assumptions can be applied. One common approach is to assume that OSBL costs amount to approximately 40% of ISBL costs. Using this assumption, we calculated the total capital costs for the capture plant, factoring in structural components, computing systems, and initial chemical feedstock. From this, OSBL costs were determined and further adjusted to include the purchased equipment cost (PEC) of compression

as well as installation expenses. Our analysis revealed that compression represents a significant portion of the overall CAPEX, substantially driving up total costs.

Material/Utility	Price \$
ISBL	
PEC (Purchased Equipment Cost)	
TOTAL ISBL	\$ 3,462,522.24
OSBL (Assumed 40% of ISBL)	
TOTAL OSBL	\$ 1,385,008.90
Compression PEC	\$ 2,428,500.00
Compression Installation	\$ 4,371,300.00
Plant Total (inc. compression)	\$ 9,218,831.14
Plant Total (no compression)	\$ 4,847,531.14

Figure 30 CAPEX of IT plant

Operating expenditures (OPEX) can be categorized into fixed and variable costs. Fixed costs, such as labor, remain constant regardless of production output, whereas variable costs, including materials, fluctuate based on production volume. In our cost model, we accounted for the necessary chemicals required to compensate for the estimated 10% solvent loss over time, as well as costs associated with waste disposal and electricity consumption for mixing.

Additionally, we included the electricity required to compress CO₂ to 1,200 psi for transport—by far the most significant contributor to operational expenses.

Fixed costs were calculated as a function of total plant costs, incorporating expenses related to maintenance and maintenance labor. Notably, our analysis highlights that the largest operating costs are associated with processes external to the core device design, particularly maintenance and compression—both of which are unavoidable expenditures in any carbon capture plant.

Reducing these costs could involve strategic plant placement in regions with lower labor expenses, rather than in high-cost urban areas. Furthermore, cost savings could be achieved by adapting alternative transport, storage, or utilization strategies. For instance, certain syngas production processes do not require high-purity, high-pressure CO₂ streams, eliminating the need for extensive compression. Alternatively, instead of compressing CO₂ for transport and then recompressing it for storage, the output stream could be injected directly into underground storage sites, minimizing energy-intensive compression steps.

OPEX Variable	\$ y-1 (24 hrs/day)
Capture Device Section	
MEA t h ⁻¹	\$ 10,441.92
DMAC t h ⁻¹	\$ 3,214.92
NCBs t h ⁻¹	\$ 19.46
Water t h ⁻¹	\$ 525.60
Waste disposal t h ⁻¹	\$ 13,929.71
Electricity kW (stirring)	\$ 2,628.00
Compression (CO₂)	\$ -
Electricity kWh	\$ 118,260.00
OPEX Fixed	
Maintenance Labor (12% of maintenance costs)	\$ 12,168.86
Maintenance (2.2% of total plant costs)	\$ 101,407.14
TOTAL PLANT OPEX	\$ 262,595.61

Figure 31 OPEX of IT Plant

With these cost estimates, we can approximate the cost per ton of CO₂ captured if the system were scaled to a 1-ton capacity. As demonstrated in the accompanying table, the cost of CO₂ capture decreases significantly as the incoming gas stream concentration increases, ranging from a 5% CO₂ environment to a 20% environment. These concentrations correspond to different industrial sources, such as natural gas processing and iron and steel manufacturing. This trend

aligns with thermodynamic principles, as it is inherently easier for the capture solution to absorb and release CO₂ from higher-concentration gas streams than from more dilute ones.

Furthermore, our analysis underscores the significant impact of compression and maintenance on overall costs. When these factors are included, the cost of capture rises dramatically, highlighting an area of ambiguity in the broader carbon capture industry. Many competitive CO₂ capture plants report costs between ~\$15 and \$130 per ton of CO₂, yet it remains unclear whether their techno-economic analyses (TEAs) fully account for compression and maintenance expenses. This lack of transparency is particularly striking given that our own estimates show these costs alone can drive the price up to \$6,000 per ton of CO₂. This discrepancy raises important questions about industry reporting practices and cost structures. However, our system appears particularly promising at higher CO₂ concentrations, with capture costs dropping to \$56 per ton at 20% flue gas concentrations—positioning it as a competitive option in industrial carbon capture applications.

Environment	ton/year (24 hrs)	\$/tCO ₂	\$/tCO ₂ (no compression)	\$/tCO ₂ (no compression, no maintenance)	\$/tCO ₂ (JUST maintenance and compression)
5%	39.0863302	\$6,718.35	\$3,692.74	\$786.97	\$ 5,931.38
7.50%	54.38098115	\$4,828.81	\$2,654.16	\$565.63	\$ 4,263.18
10%	253.2114435	\$1,037.06	\$570.02	\$121.48	\$ 915.58
15%	314.3900472	\$835.25	\$459.10	\$97.84	\$ 737.42
20%	543.8098115	\$482.88	\$265.42	\$56.56	\$ 426.32

Figure 32 Estimated cost per ton of CO₂ in varying environmental saturation regimes

As part of our TEA, we sought to explore the feasibility of scaling the PPC system beyond the 1-ton capacity to a level equivalent to 1 million tons per annum (1 Mtpa) of CO₂ capture—a

benchmark often considered "pilot scale" in CCS projects. While cost considerations were a crucial factor, we also aimed to evaluate the material and spatial requirements necessary to support such a scale. Based on reaction rates and system efficiency, regenerating 1 Mtpa of CO₂ from a 5% flue gas stream would require an astonishing 1.96×10^{11} liters of capture solution. This sheer volume alone presents a significant challenge.

To better visualize the physical footprint required, we mapped out the land area needed to accommodate the system. For a 5% CO₂ environment, the required area would be equivalent to the size of an entire county in North Dakota—an impractically large expanse for a single carbon capture installation. Even under a more concentrated 20% CO₂ stream, the land and material requirements remain substantial, demanding vast quantities of sorbent across an enormous plot of land. While our analysis shows that the cost per ton of CO₂ capture remains relatively low, the system's spatial and material demands pose a major scalability issue.

This finding highlights a fundamental flaw that is often overlooked in carbon capture system design: the excessive volume required for solvent regeneration and the significant land footprint necessary for implementation. Moving forward, efforts must focus on reducing both the volume of capture solution required and the overall spatial demands of a scaled-up system. Identifying ways to enhance solvent efficiency, increase CO₂ loading capacity, and optimize system architecture will be critical to making this approach viable for large-scale deployment.

Environment	Vol. Scale Factor	Vol. Req. 1 MTPA (L)	Radius (m)	Area (m ²)	Area (km ²)
5%	1.96E+13	1.96E+11	2.49E+08	1.95E+17	1.95E+11
7.50%	1.30E+13	1.30E+11	1.66E+08	8.68E+16	8.68E+10
10%	2.45E+12	2.45E+10	3.12E+07	3.05E+15	3.05E+09
15%	1.96E+12	1.96E+10	2.49E+07	1.95E+15	1.95E+09
20%	1.12E+12	1.12E+10	1.42E+07	6.38E+14	6.38E+08

Table 4 Volume of capture solution required for 1 Mtpa

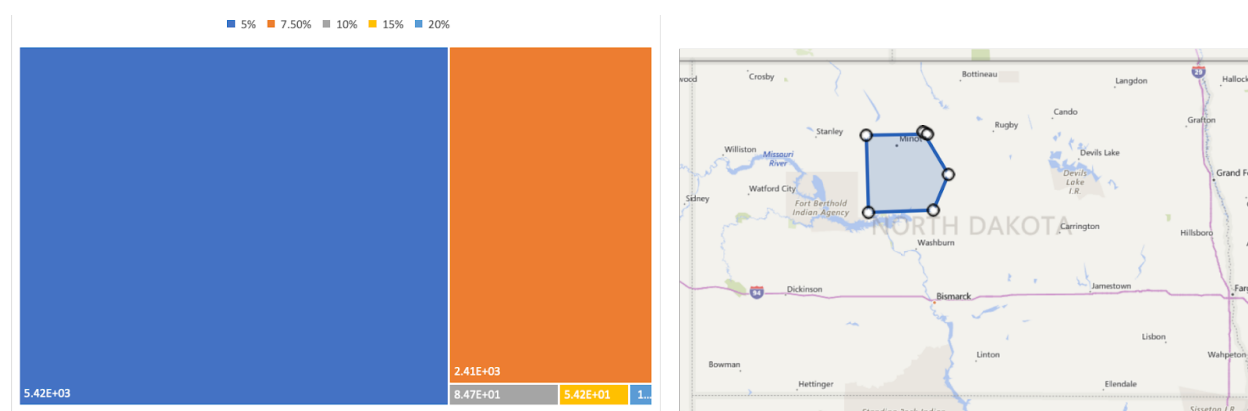


Figure 33 Area required for 1 Mtpa

2.7 Conclusions from PPC Device

We have demonstrated a bench-scale device that has taken advantage of an established photothermal chemistry to facilitate passive carbon capture. Ideally, this device would be used in an industrial setting for point-source capture due to its high efficiencies in environments with 10-30% CO₂. We have demonstrated that this device can be run solely from solar energy with the aid of a Fresnel lens or another light-enhancing optical tool. We have found that the device works well with DMAC and water and MEA. However, other solvents are more efficient,

including methanol. The device could be improved by further developing porous membranes for gas exchange. Omniphobic membranes are a potential solution which could decrease membrane wetting and degradation over time. Additionally, it will be important to generate a consistent capture solution temperature from the sun. Long term light cycling, such as day-to-night loading and release could be a potential large-scale testbed which would provide insight into the scalability of the device.

While the laboratory results demonstrate proof-of-concept, a key challenge lies in scaling up the device for industrial applications. In particular, issues such as membrane longevity, consistent light cycling, and material degradation under harsh industrial conditions must be addressed. The device's current design prioritizes optimizing the surface area of photothermally active amine solution exposed to sunlight, but achieving this at scale without efficiency losses remains a major research focus. Future prototypes will need to incorporate advanced materials capable of sustaining continuous use without compromising regeneration rates. While the efficiency of this bench-scale model (4.42 mol CO₂/MJ) is comparable to existing technologies, further analysis is required to confirm its viability in larger industrial settings.

3 Development of High Contact Photothermal (HCP) Device

While our first prototype (PPC) successfully regenerated CO₂ from flue gas streams containing up to 30% CO₂, it struggled to regenerate CO₂ in statistically significant quantities from ambient air, where CO₂ levels are just 0.04%. Although the device operated efficiently with minimal energy demands for regeneration, other costs posed significant challenges. These included fixed

costs such as compression, labor, waste disposal, and solvent loss. A major limitation of the PPC was the large volume of sorbent required to scale the system to pilot size. This inefficiency stemmed from the prototype attempting to perform two processes—absorption and desorption—that ideally require different operating conditions. Furthermore, the device failed to optimize contact between the sorbent and the membrane, further limiting its effectiveness.

To improve upon the PPC, we developed a new system—the High Contact Photothermal (HCP) Device—which addresses its shortcomings by incorporating a flow-based design to enhance CO₂ capture and regeneration efficiency. Unlike the PPC, which did not rely on pumps to move sorbents through the system, we found that incorporating pumps had a minimal impact on overall energy costs. A pump-based system—or potentially a sunlight-driven fluid system—enabled CO₂ capture fluids to interact with the feed gas stream under one set of conditions (30–50°C) and release CO₂ under another (80°C). While this approach is similar to existing industrial designs for CO₂ stripping from flue gas, it leverages photothermal release to operate with reduced space requirements and smaller volumes of capture fluid, making the system more efficient and compact.

One of the primary advantages of implementing a sunlight-driven capture system is its versatility and scalability, allowing it to be deployed almost anywhere. Current industrial flue gas sources, such as cement and steel manufacturing facilities or oil and gas refineries, are typically integrated into the energy grid with robust infrastructure already in place. While coupling these systems with sunlight could help offset their overall energy demand, the true potential of a photothermal capture system lies in its ability to operate efficiently in locations without

extensive energy infrastructure. This makes it particularly advantageous for regions where large-scale energy buildouts are not feasible or available.

This is where direct air capture (DAC) becomes particularly relevant. DAC systems are designed to remove CO₂ from ambient air, and these facilities are often located away from large cities due to the significant space required for air contact. To further reduce costs, it's advantageous to position DAC facilities closer to CO₂ storage sites, minimizing transportation expenses. The HCP device aims to maximize its suitability for DAC, leveraging its ability to use sunlight as a direct energy source.

3.1 Determining HCP Components

3.1.1 Membrane material selection

While expanded polytetrafluoroethylene (ePTFE) was selected as the membrane material for the Passive Photothermal Capture (PPC) device due to its hydrophobicity, chemical resistance, and stable morphology under operating conditions, the Hollow Contactor Photothermal (HCP) device posed a distinct set of challenges. In particular, concerns regarding membrane wetting, chemical compatibility with amine-based capture solutions, and thermal stability prompted a broader survey of potential hollow fiber materials.

Unlike the PPC setup where membrane sheets are employed, the HCP device requires small-diameter hollow fibers—materials that are less broadly available in a porous format. Moreover,

given the increased surface area for gas-liquid exchange, we hypothesized that fibers with smaller pore sizes might suffice, provided they retained porosity and resistance to fouling under operational conditions. Thus, we selected four candidate materials available in tubular form for preliminary evaluation: ultra-high molecular weight polyethylene (UHMW-PE), expanded PTFE (ePTFE), microporous polyethersulfone (mPES), and polydimethylsiloxane (PDMS).

3.1.1.1 Membrane Release tests

To determine whether various membrane materials were compatible with our system and could operate effectively with a nanosolution containing carbon black, we benchmarked several candidates for their ability to release CO₂ upon heating. A suitable membrane would act as an effective interface between the liquid and gas phases, allowing CO₂ to pass through for collection after desorption.

The experimental setup is outlined in Figure 34. A reservoir was filled with 200 mL of our stock capture solution (30% MEA with 0.2 wt% NCBs) and sparged with a constant stream of pure CO₂ for two hours to ensure saturation. Using a peristaltic pump set to 1 mL/min, the solution was circulated through the test system. First, it passed through a glass heating arm irradiated by a lamp, then through membrane tubing where CO₂ was expected to be released. CO₂ concentration was measured downstream of the membrane to assess its gas-release performance.

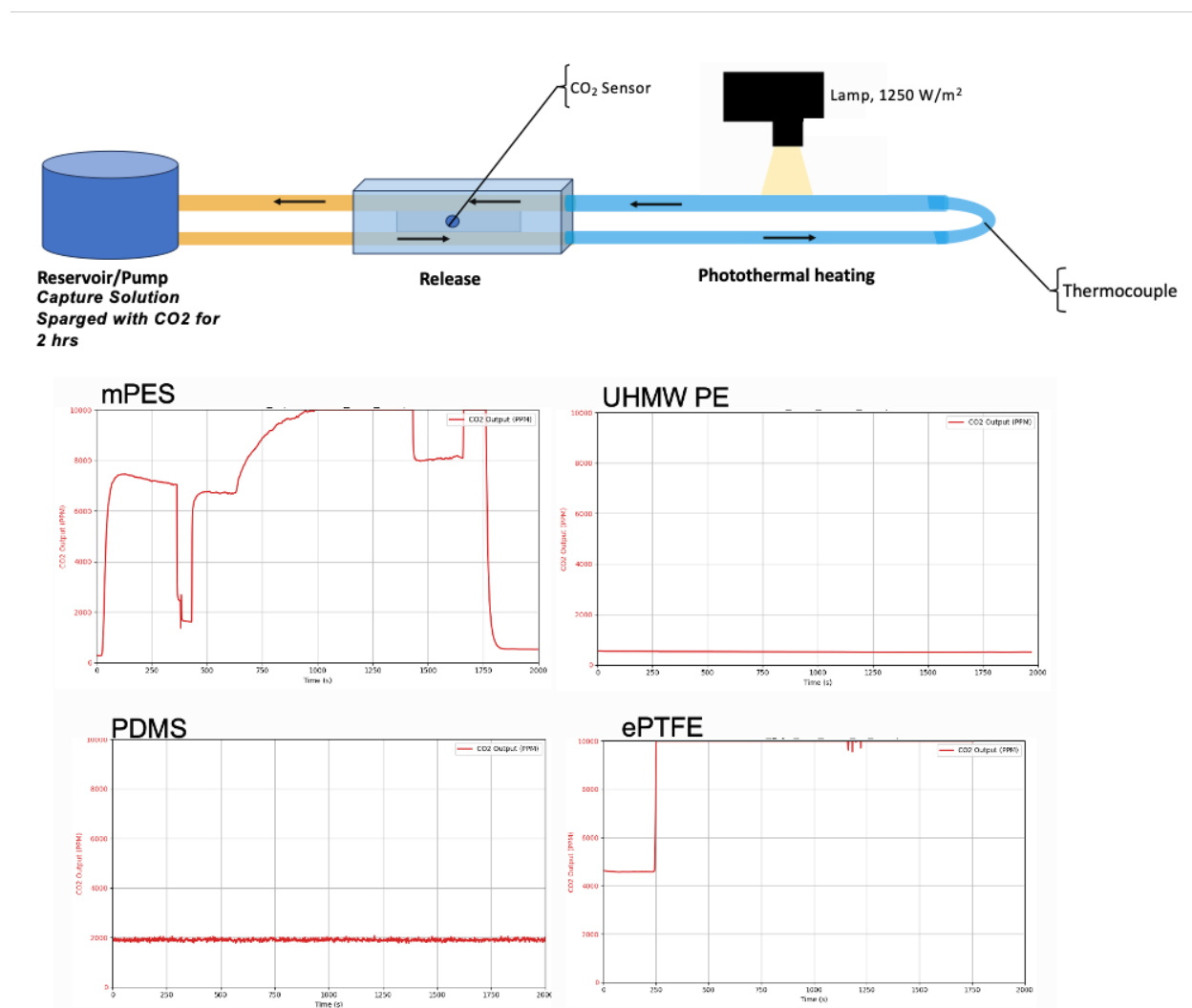


Figure 34 Experimental results for determining effective release of CO₂ through membrane materials

The results showed that both modified polyethersulfone (mPES) and expanded polytetrafluoroethylene (ePTFE) successfully released CO₂ from the solution, as indicated by the sharp spikes in measured CO₂ concentrations (Figure 34). In contrast, ultra-high molecular weight polyethylene (UHMW PE) and polydimethylsiloxane (PDMS) did not demonstrate CO₂ release, possibly due to unfavorable pore size or excessive membrane thickness. Based on these results, mPES and ePTFE are currently the most promising candidates for membrane selection.

3.1.1.2 Membrane fouling tests

To simulate realistic operating conditions, we prepared a test solution consisting of 30 wt% monoethanolamine (MEA) and 0.2 wt% nanocarbon black (NCB) dispersed in water, and maintained the solution at 85°C. Each hollow fiber material was exposed to continuous flow of 20 mL/min of this solution for 24 hours. Following exposure, the fibers were collected and analyzed using scanning electron microscopy (SEM) to assess morphological stability, pore retention, and the extent of fouling.

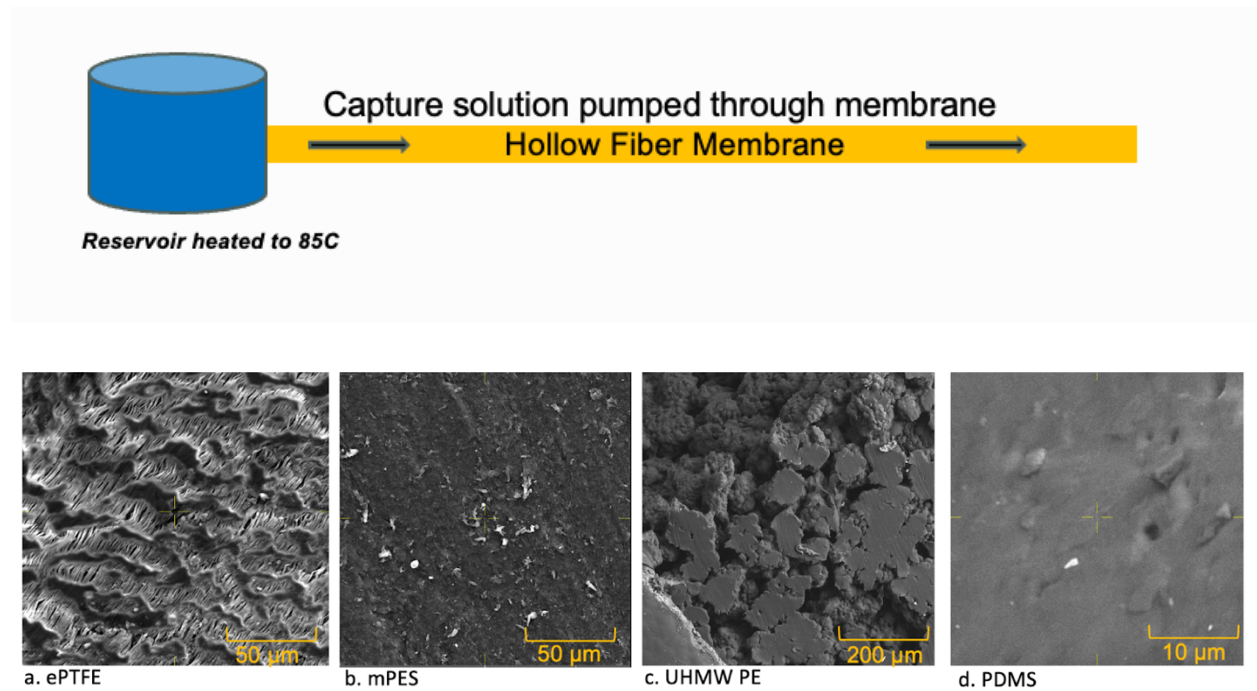


Figure 35 Experimental results of membrane fouling tests for ePTFE, mPES, UHMW PE, and PDMS

The UHMW-PE fibers exhibited the most severe degradation. Rather than a well-defined porous structure, the SEM images revealed irregular, agglomerated morphologies lacking uniform pore architecture, potentially due to thermal swelling and pore collapse. This suggests that the non-uniform structure of UHMW-PE is incompatible with sustained exposure to heated MEA-NCB systems.

The mPES fibers retained some of their original porous structure after exposure, but visible signs of degradation and pore obstruction were evident. The observed fouling may be attributable to chemical interactions between the amine solution and the membrane, or physical entrapment of carbon black particles.

PDMS fibers demonstrated complete fouling after the 24-hour test period. Given their relatively large nominal pore size ($\sim 2\ \mu\text{m}$), the SEM images showed most surface pores completely filled with NCB aggregates and solution residue. This indicates poor anti-fouling performance under these specific operating conditions.

In contrast, the ePTFE fibers displayed the highest degree of structural integrity post-exposure. While some fouling and minor degradation were observed, the characteristic microporous network remained largely intact. This result reinforces ePTFE's suitability as a membrane material for long-term operation in photothermal CO_2 capture systems using aqueous MEA-NCB solutions at elevated temperatures.

3.1.1.2 Effect of NCBs on Fouling

Understanding the impact of carbon black (NCBs) on membrane surface morphology was also a critical aspect of system development. To investigate this, we repeated the earlier experiment—pumping capture solution through the membrane materials at 20 mL/min for 24 hours—but compared the performance and surface characteristics of 30% MEA solutions with and without

0.2 wt% NCBs. These trials were conducted using the two more promising membrane materials identified previously: ePTFE and mPES.

The results revealed a clear distinction between membranes exposed to NCB-containing solutions and those exposed to NCB-free solutions. In the case of ePTFE, while the MEA solution without NCBs caused minimal surface changes, the addition of NCBs led to partial pore blockage and visible stretching or distortion of the membrane pores. However, many pores remained available, suggesting that ePTFE retains some level of function even when challenged by nanoparticle-containing solutions.

In contrast, the mPES membrane exhibited more substantial interaction with NCBs. Although some pore buildup was observed with the MEA-only solution, the presence of NCBs led to almost complete surface coverage, likely impeding CO₂ release. This difference may be attributed to varying charge distributions or surface chemistries between the membranes, affecting their affinity for carbon black particles. Overall, ePTFE appeared to be more compatible with NCB-based solutions than mPES, although both materials may experience some degree of degradation or fouling over time due to nanoparticle interactions.

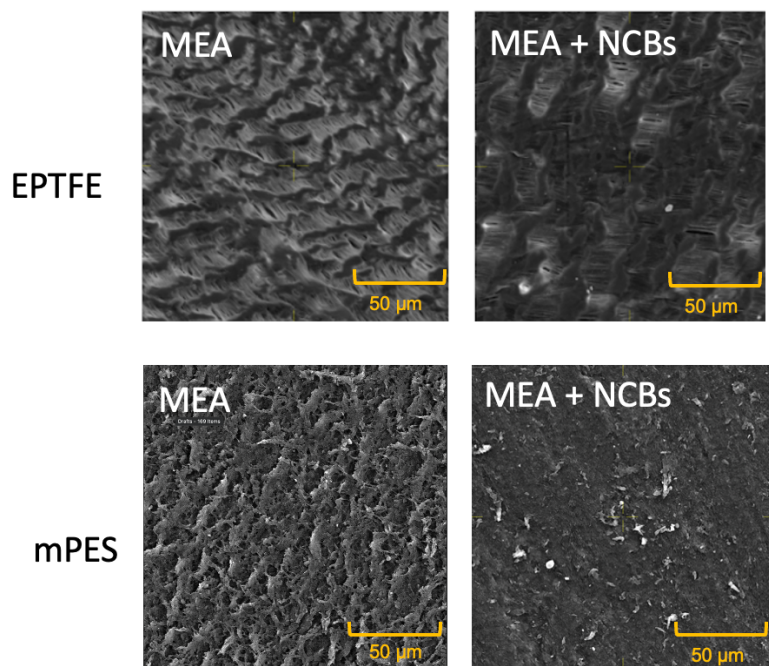


Figure 36 SEM images of EPTFE and mPES after undergoing capture solution flow for 24 hours

These initial findings suggest that membrane selection is critical for maintaining HFMC performance under photothermal operating conditions, and that ePTFE offers superior resistance to thermal and chemical fouling in this context.

3.1.2 Determining DAC Capture Solution

The capture solution used in the previously developed PPC device consisted of a 30% solution of monoethanolamine (MEA) in water and dimethylacetamide (DMAC) with 0.2 wt% carbon black nanoparticles (NCBs). While this solution demonstrated strong performance in that setup, our goal for the DAC device was to evaluate alternative sorbents that could optimize performance under direct air capture conditions. Unlike earlier experiments that utilized CO₂-enriched feed

streams, the DAC setup relies exclusively on ambient air, presenting a greater challenge due to the lower CO₂ concentration. Therefore, we aimed to identify sorbents that are (1) highly selective for CO₂ at low partial pressures, (2) less volatile than MEA to prevent evaporation and decomposition, and (3) chemically and physically compatible with the photothermally active NCBs used in the system.

3.1.2.1 CO₂ Regeneration from Air Feed-Gas

To identify suitable sorbents for this application, we conducted an initial screening process. Previous research has shown that among aqueous amines, primary and secondary amines tend to exhibit superior performance in CO₂ capture. The efficiency of aqueous alkanolamine solutions in absorbing CO₂ is closely linked to their chemical structure and the species formed during the absorption reaction. Unhindered primary amines, such as MEA, are particularly well-suited for DAC due to their high efficiency and lower energy requirements for sorbent regeneration, as they operate effectively at reduced regeneration temperatures.

For this study, we aimed to expand beyond MEA and test other primary and secondary amines with potentially higher CO₂ absorption capacities. The amines selected for evaluation included MEA, diglycolamine (DGA), and methylmonoethanolamine (MMEA). These candidates were assessed based on their pK_b values, percentage of CO₂ absorbed over a 24-hour period, and total moles of CO₂ absorbed in the same timeframe. The results of this screening are summarized in the table below:

Table 5 Aqueous amines suitable for DAC

Amine	pK _b at 25°C	abs% at 24 hr (%)	CO ₂ abs at 24 hr (mol)
MEA	4.49	87.4	0.0175
DGA	4.38	84.8	0.0172
MMEA	4.12	89.1	0.0178

In addition to aqueous amines, we explored amino acids as potential sorbents for DAC. While aqueous amines exhibit excellent CO₂ capture capabilities, they also present challenges that make them less ideal for direct air capture. For instance, amines tend to volatilize when exposed to airflow, which is a significant drawback for long-term DAC operations. Furthermore, they are often toxic and degrade at temperatures that closely align with the conditions required for regeneration. Amino acids, on the other hand, offer several advantages. They are less volatile, non-toxic, biodegradable, simple to synthesize, and more resistant to thermal degradation compared to aqueous amines.

For this study, we tested potassium glycinate (K-GLY) and potassium lysinate (K-LYS) due to their high CO₂ loading capacities, which range from 0.4–1.4 mol/mol for K-GLY and 0.66–1.7 mol/mol for K-LYS. These amino acids present a promising alternative to traditional amine-based sorbents for DAC applications, combining environmental compatibility with high CO₂ absorption potential. Further details on the experimental methods and results for both amine and amino acid sorbents are discussed later in this work.

In these experiments, we evaluated the regeneration behavior of various capture solutions, both with and without carbon black (NCBs). Distinct from prior experiments that used pure CO₂ for loading, these trials relied solely on ambient air as the CO₂ source, making the results more representative of real-world, low-concentration capture scenarios. For each trial, 10 mL of the capture solution was placed in a round-bottom flask and sparged with air for two hours. The tested solutions included 30% MEA in water, 1.5 M MMEA, 1.5 M DGA, 1 M GLY-K, and 1 M LYS-K. When used, NCBs were added at a concentration of 0.2 wt% and sonicated to ensure even dispersion. After loading with CO₂, the regeneration step was conducted under two different conditions: solutions without NCBs were heated to 100 °C using a sand bath, while those containing NCBs were irradiated with a lamp to induce photothermal regeneration. The results of these comparative trials are described below.

Table 6 Regeneration of CO₂ from air using MEA, MMEA, DGA, LYS-K, and GLY-K

Solution	CO₂ Output (mols)	Regen. Temp (C)
MEA	4.5E-4	94
MEA + NCBs	2.5E-5	66
MMEA	(n/a)	(n/a)
MMEA + NCBs	(n/a)	(n/a)
DGA	(n/a)	(n/a)
DGA + NCBs	5.6E-5	55
LYS-K	(n/a)	(n/a)
LYS-K + NCBs	(n/a)	(n/a)
GLY-K	2.9E-5	115
GLY-K + NCBs	4.6E-5	67

These results led us to prioritize DGA and GLY-K as the most promising sorbents for our DAC system. As shown in Table X, MMEA and LYS-K did not regenerate any measurable CO₂ under ambient conditions, regardless of temperature. To explore whether this was due to insufficient basicity, we attempted to enhance the LYS-K solution by adding 2 M KOH in a 1:1 ratio. However, this adjustment did not improve CO₂ regeneration. Similarly, MMEA showed no regeneration, which could suggest a pressure or humidity requirement that our ambient air setup does not meet.

In contrast, DGA, GLY-K, and MEA all released some CO₂ after air sparging and subsequent heating, indicating their potential viability. Notably, DGA did not regenerate CO₂ with heat alone but did so effectively when NCBs were included, suggesting a strong photothermal enhancement. MEA, however, regenerated more CO₂ when heated without NCBs than with them—an unexpected result, as previous experiments using CO₂-enriched air had shown higher regeneration with NCBs present. This discrepancy may be due to the differences in gas composition and flow rate: with ambient air, greater volumes are required to achieve comparable CO₂ exposure, and additional components in the air may interfere with sorbent performance. GLY-K also demonstrated improved regeneration under photothermal conditions, with higher moles of CO₂ released compared to thermal-only heating. Overall, DGA had the most promising performance, achieving CO₂ regeneration at relatively low temperatures (~55 °C) and yielding the highest CO₂ output among the tested sorbents.

3.1.2.2 Sorbent Interaction with EPTFE

Another important factor we considered was the compatibility of the new capture solutions with the membrane materials. While we had already characterized the interaction between ePTFE and MEA with NCBs, we had not yet evaluated how ePTFE would perform with GLY-K and DGA. To assess this, we conducted the same experimental procedure described previously: each solution was heated and pumped through ePTFE hollow fiber membranes continuously for 24 hours. We then analyzed the membranes using SEM to evaluate any morphological changes or material degradation.

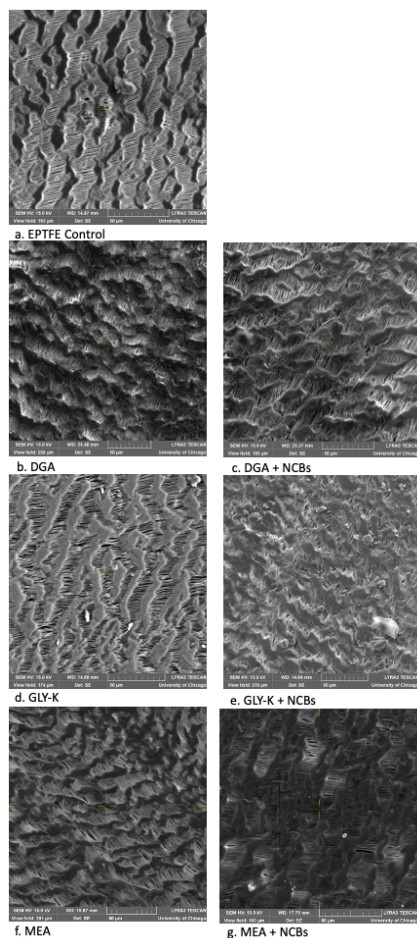


Figure 37 SEM Images of ePTFE after running with capture solutions

The SEM images, all scaled to 50 μm , reveal different impacts of the sorbents on EPTFE.

In the EPTFE control, the striations in the PTFE are clear and well-defined, with distinct gaps that may facilitate gas and sorbent exchange. Comparing this to the membranes exposed to various sorbents for 24 hours at 80°C, we observe noticeable changes. While every capture solution appears to affect the overall structure of the EPTFE, these effects seem to be primarily physical rather than indicative of chemical denaturation or fouling. The striations appear less uniform and more distorted than those in the control, and the individual threads seem slightly swollen due to exposure to the solution.

Among the tested solutions, GLY-K without NCBs had minimal impact on membrane morphology and showed little evidence of fouling or clogging. However, when NCBs were introduced, the surface of the membrane exhibited substantial buildup, partially obscuring the original texture.

Both DGA and MEA showed similar behavior, with moderate surface deposition in the absence of NCBs and increased accumulation when NCBs were included. The most pronounced morphological changes were observed in samples exposed to carbon black-containing solutions.

These membranes displayed large agglomerates of material embedded in and around the pores, indicating a likely seeding and aggregation mechanism driven by the nanoparticles. These findings suggest that carbon black may promote time-dependent fouling behavior, and further study is warranted to understand its kinetics and long-term effects on membrane performance.

From these studies, MEA, DGA, and GLY-K all appear to be promising sorbents for use in this system. However, moving forward, it may be beneficial to explore alternative methods of photothermal heating that do not rely on pumping nanosolutions of carbon black, as this approach seems to contribute to progressive fouling of the ePTFE membrane over time. This is a notable drawback, as carbon black significantly enhances CO₂ release for both GLY-K and DGA. While its performance benefits are clear, the potential for membrane clogging is a key limitation. Strategies to mitigate this issue—such as surface modification of the ePTFE to reduce

particle adhesion or functionalizing the carbon black nanoparticles to prevent aggregation—could be worthwhile areas of investigation.

3.2 Building HCP Device

With the individual components of the system now characterized, and a clearer understanding of sorbent–membrane interactions established, the next phase of this work involved integrating these components into a functional direct air capture (DAC) prototype. Two primary conclusions emerged from the preceding studies. First, suitable sorbent solutions for this system include 30% MEA, 1.5 M DGA, or 1 M GLY-K, with the addition of carbon black nanoparticles (NCBs) shown to enhance photothermal regeneration performance, albeit with some risk of membrane fouling. Second, ePTFE emerged as the most compatible membrane material, although mPES may serve as a viable alternative if clogging from NCBs can be mitigated. Based on these findings, the subsequent design of the DAC prototype aimed to maximize gas–liquid contact, promote efficient CO₂ uptake and release, and accommodate photothermal heating while minimizing system degradation over time.

3.2.1 mPES Hollow Fiber Membrane Contactor

To evaluate the feasibility of employing hollow fiber membrane contactors (HFMCs) within the designed gas-liquid absorption system, initial experiments were conducted using commercially available HFMCs. Given that this approach had not previously been tested within our setup, we prioritized accessibility and time efficiency over full customization in the preliminary phase.

Fabricating HFMCs in-house is a time-intensive process, and before investing substantial effort into module construction, it was necessary to confirm the compatibility and basic functionality of HFMCs within our system architecture.

To this end, off-the-shelf HFMC modules were procured for initial trials. The primary advantage of using these commercial modules was their immediate availability and replaceability.

However, this came with the tradeoff of limited control over membrane geometry, material selection, and module configuration, which could influence mass transfer performance and long-term chemical compatibility.

Due to supply chain constraints at the time of purchase, the only suitable commercial option identified was a COBETTER HFMC model. These contactors utilized microporous polyethersulfone (mPES) hollow fibers with an inner diameter of 1 mm, housed within a rigid polysulfone casing. Each module measured approximately 30 cm in length and contained between 3 to 6 hollow fiber membranes. Although not specifically optimized for our application, these modules were deemed sufficiently representative to test overall system compatibility, gas flow behavior, and preliminary mass transfer performance under relevant operating conditions.



Figure 38 Image of COBETTER mPES Hollow Fiber Membrane Contactor

3.2.2 Hollow Fiber Membrane Contactor Fabrication

Hollow fiber membrane contactors (HFMCs) are widely used in gas-liquid separation and absorption applications due to their high surface area-to-volume ratios and modularity. However, the fabrication of HFMC modules presents several practical challenges, particularly during the potting process (63). One critical consideration is the prevention of pore blockage or fiber lumen obstruction by potting materials, which can compromise gas flow and mass transfer efficiency (72). Previous studies have highlighted this issue as a significant bottleneck in HFMC assembly, necessitating refined techniques to ensure open lumens and mechanically stable configurations. This work presents a practical method for constructing custom HFMCs using expanded polytetrafluoroethylene (ePTFE) hollow fibers, with careful attention paid to lumen preservation during potting.

To fabricate the HFMCs, ePTFE hollow fiber membranes with internal diameters (ID) of 0.5 mm and 1 mm were procured from the supplier Yufreyoo. Two modules were constructed with different geometries. For the first module, eight fibers with 1 mm ID were cut to a length of 8 inches. For the second module, 28 fibers with 0.5 mm ID were cut to 12 inches in length. To prevent collapse of the fiber lumens during potting and to add structural integrity, stainless steel wires were temporarily inserted into the inner lumens of each fiber.

The potting process involved vertically positioning the bundle of fibers through a 1.5” diameter stainless steel ferrule, which was then placed inside a 250 mL glass beaker. A low-melting-point sacrificial support material, polyethylene glycol (PEG), was selected to fill the lower section of the ferrule and temporarily stabilize the fibers. Approximately 50 mL of PEG was melted at 150 °C for 20 minutes and poured into the beaker to a level coinciding with the ferrule lip. This was allowed to cool and solidify, embedding the fibers in place. After one hour, the remaining volume of the ferrule lip was filled with two-part epoxy resin to form a permanent potting seal. The epoxy was cured at room temperature for 3 hours. The PEG was then removed by immersing the assembly in a hot water bath maintained at ~90 °C for 1 hour, which dissolved and released the sacrificial PEG, leaving the fiber lumens open and embedded solely in epoxy.

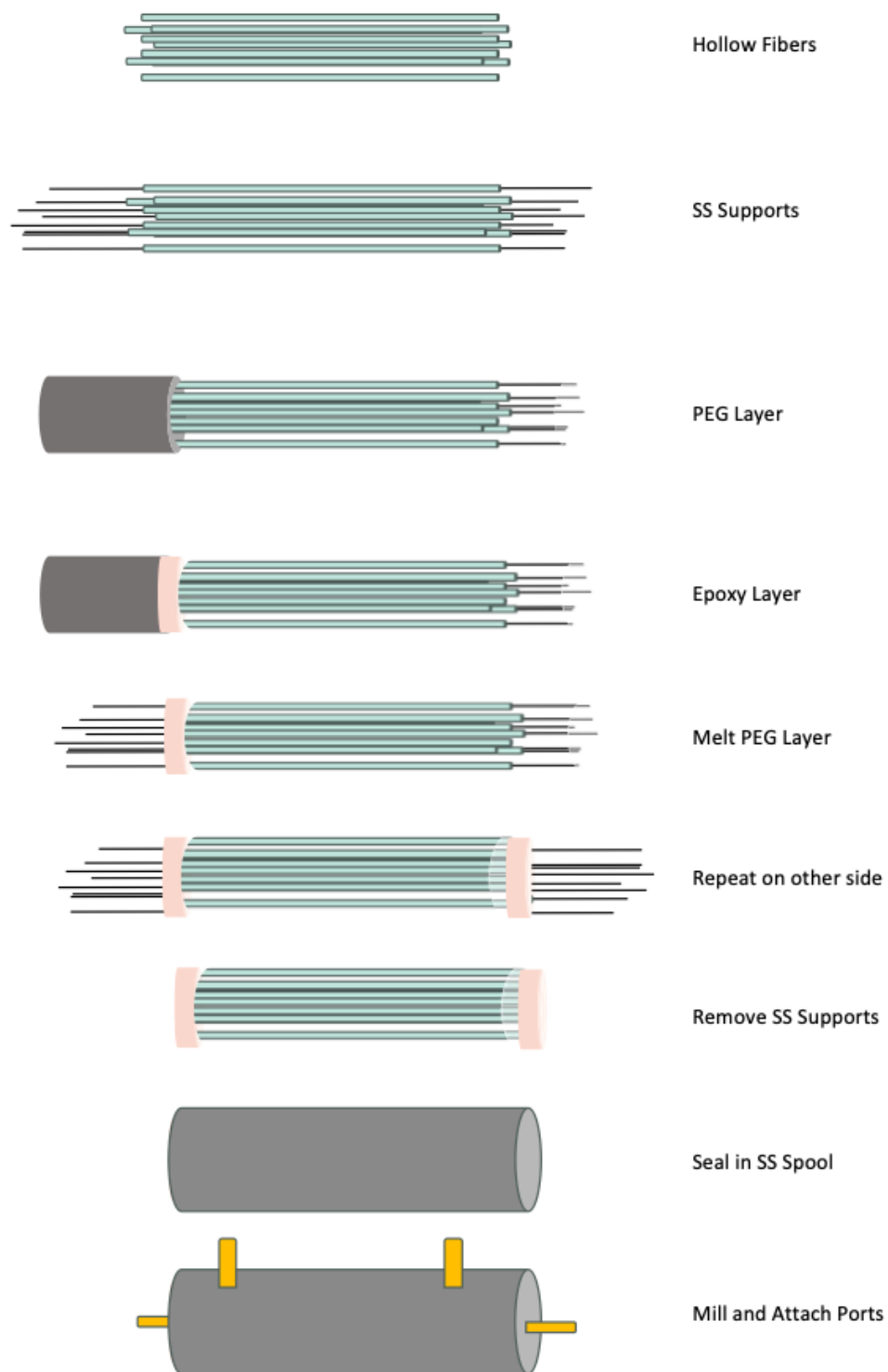


Figure 39 Fabrication of ePTFE HFMC

After potting one end, the fibers were passed through a custom-fabricated stainless steel housing (1.5” internal diameter, 6” length), sealed with rubber gaskets. The housing was fitted with two ¼” port adapters for air-side flow, with the shell side used for liquid capture solution. The same potting procedure was repeated on the opposite end of the fibers, ensuring alignment and sealing within the second ferrule. Triclamp connectors were used to couple the ferrules, stainless housing, and inlet/outlet flow adapters, completing the assembly of a functional hollow fiber membrane contactor. This modular setup enabled controlled and leak-tight integration of HFMCs into the test apparatus.

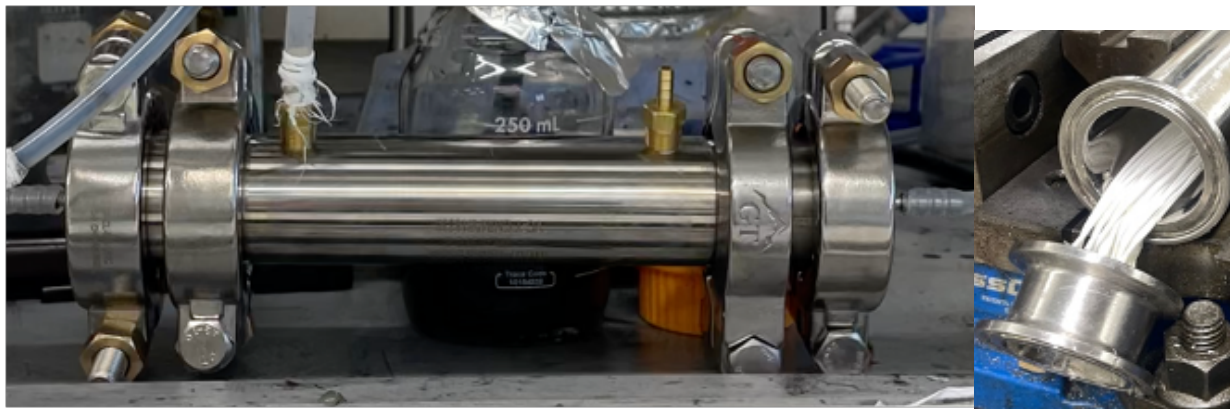


Figure 40 Image of ePTFE HFMC

3.3 HFMC Performance Testing

To evaluate the effectiveness of hollow fiber membrane contactors (HFMCs) for both CO₂ absorption and desorption, a series of initial experiments were conducted using both commercial microporous polyethersulfone (mPES) HFMCs and custom-fabricated expanded polytetrafluoroethylene (ePTFE) HFMCs. The goals of these experiments were twofold: (1) to

determine whether the HFMCs could effectively facilitate CO₂ loading into a capture solution from air, and (2) to assess their ability to release CO₂ from CO₂-rich capture solution during thermal regeneration.

3.3.1 HFMC Loading Tests

To test CO₂ loading, ambient air (house air supply) was passed through each HFMC at a flow rate of 1 L/min for two hours. Simultaneously, a 30 wt% monoethanolamine (MEA) aqueous solution containing 0.2 wt% nanocarbon black (NCB) was pumped countercurrently through the shell side of the contactor. Two liquid flow rates were evaluated: 1 L/min and 15 mL/min, in order to assess the effect of residence time and flow dynamics on CO₂ mass transfer. After this loading process, the capture solution was collected in a 50 mL round-bottom flask and subjected to thermal regeneration by heating to 100 °C in a sand bath. The released CO₂ was quantitatively measured to assess the loading performance of each membrane type.

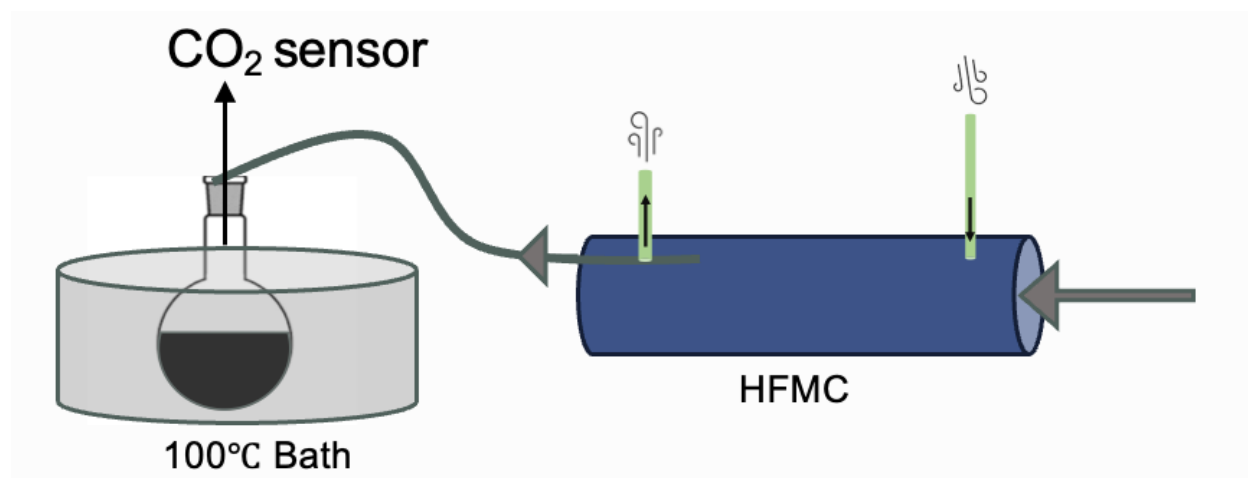


Figure 41 Experiment setup to test loading capability of HFMC

Results indicated that the ePTFE-based HFMC was effective at promoting CO₂ uptake into the capture solution. Notably, lower liquid flow rates (15 mL/min) resulted in significantly higher CO₂ absorption compared to the higher flow rate condition (1 L/min). This outcome is consistent with expectations, as lower flow rates increase the residence time of the solution within the contactor and may reduce turbulence, thereby enhancing gas-liquid interaction and mass transfer. From an energy efficiency perspective, this is advantageous, as reduced pumping energy is required at lower flow rates.

In contrast, the commercial mPES HFMC did not demonstrate measurable CO₂ regeneration following the same loading and heating procedure. The negligible CO₂ desorption observed suggests that this membrane type may be less permeable to CO₂ or otherwise inhibits efficient gas-liquid contact under the experimental conditions. These differences are likely attributable to variations in membrane material properties, including porosity, wettability, and gas diffusivity. From these findings, we concluded that (1) lower liquid flow rates are favorable for maximizing CO₂ uptake in HFMC-based systems, and (2) ePTFE membranes are more effective for CO₂ loading than the tested mPES membranes, at least under the conditions studied. These insights guided subsequent optimization of contactor design and operating parameters in the system.

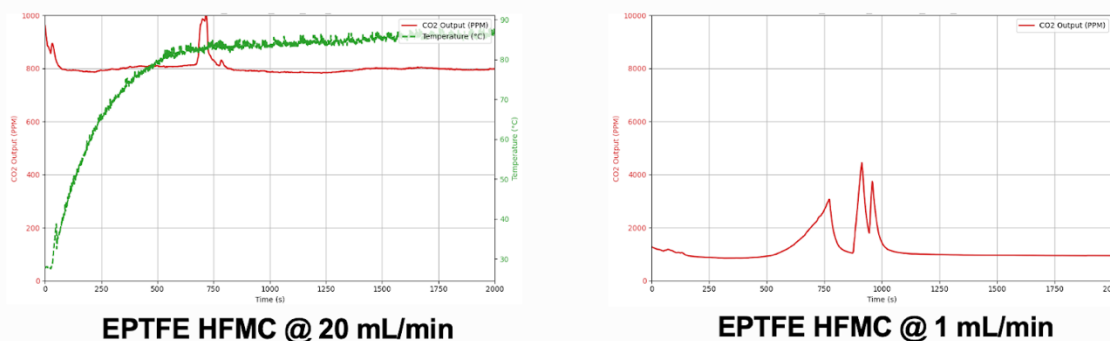


Figure 42 Results of loading test of EPTFE HFMC

3.3.2 HFMC Release Tests

In addition to CO₂ absorption, the effectiveness of HFMCs as reactors for CO₂ desorption was assessed. In the overall system design, thermal regeneration of the CO₂-loaded capture solution occurs in HFMC #3, where the solution is heated to release CO₂. To identify the optimal HFMC for this step, a series of experiments were conducted using preloaded capture solution to evaluate the relative performance of commercial mPES and custom-fabricated ePTFE HFMCs.

Capture solutions were first saturated with CO₂ by direct bubbling prior to use in this experiment. These preloaded solutions were then passed through a photothermal heating arm, where they were exposed to continuous irradiation from a near-infrared (NIR) lamp to simulate the thermal conditions of regeneration. After heating, the solution flowed through the lumen side of the HFMC. Simultaneously, a sweep gas of nitrogen (N₂) was passed countercurrently through the shell side of the contactor. The outlet gas from the HFMC shell was directed to a CO₂ sensor for continuous monitoring.

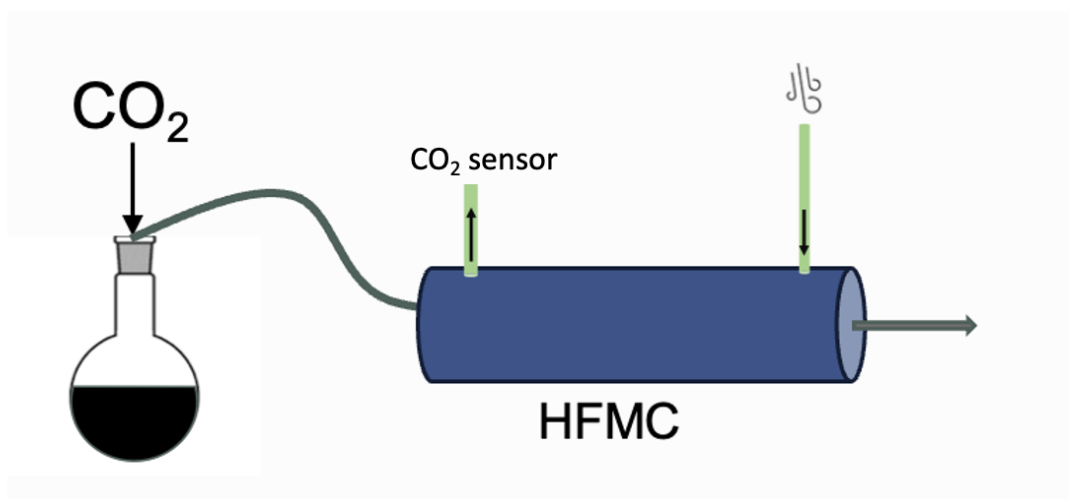


Figure 43 Schematic of release test for HFMC

Interestingly, the mPES HFMC exhibited significant CO₂ desorption. CO₂ was detected at the outlet even before the capture solution reached the intended regeneration temperature, suggesting that the membrane's properties or physical configuration may facilitate early CO₂ release. In contrast, the ePTFE HFMC did not yield similarly high CO₂ output under identical experimental conditions.

This discrepancy is particularly notable given the earlier finding that the ePTFE HFMC was more effective for CO₂ loading. The reduced apparent CO₂ release observed in the ePTFE system is likely attributable to its larger shell volume. The custom-built ePTFE HFMCs used stainless steel spools with substantially higher internal volume than the compact polysulfone housing of the mPES HFMCs. As the volume of gas exiting the ePTFE shell was diluted by the larger headspace and lower relative concentration of desorbed CO₂, the output signal at the CO₂ sensor was less pronounced.

Therefore, while the ePTFE HFMC likely did facilitate CO₂ release, its performance in this specific configuration was masked by geometric and flow-related dilution effects. These findings underscore the importance of contactor geometry and shell-side volume when evaluating membrane performance for CO₂ desorption and highlight the suitability of the more compact mPES HFMCs for small-scale, low-volume thermal regeneration steps.

3.3.3 Heat Exchange in HFMC

One of the functions of the hollow fiber membrane contactors (HFMCs) in the HCP device is to facilitate both heat and solute (CO₂) exchange. In the context of this system, which is designed to operate under low CO₂ concentration environments such as ambient air, the HFMCs are investigated for their potential to enhance CO₂ enrichment in the output stream through countercurrent amplification. This involves passing a CO₂-rich stream, originating from the loading HFMC, in a countercurrent configuration against a lower-concentration stream that has already undergone CO₂ desorption in the photothermal regeneration arm. This counterflow not only aids in concentrating CO₂ but also enables thermal energy exchange.

Specifically, because the sorbent solution must be cooled to approximately 25 °C during the CO₂ loading step and subsequently heated to as high as 80 °C during the release step, a substantial temperature shift is required throughout the process. The HFMC serves as a passive mechanism for thermal coupling, transferring heat from the hot, regenerated stream to the incoming cooler stream. This reduces the total external energy input required for heating and simultaneously brings the cooled stream closer to the desired temperature for CO₂ uptake. Thus, the HFMC

plays a dual role in enhancing both the energetic efficiency and mass transfer dynamics of the overall system.

To evaluate the heat exchange dynamics of the HFMC within the integrated system, we constructed an experimental setup designed to reflect anticipated real-world operating conditions. Specifically, we circulated a capture solution consisting of 30% monoethanolamine (MEA) with 0.2 wt% carbon black nanoparticles (NCBs) through the HFMC and then into the photothermal arm, which was directly irradiated with a lamp providing an intensity of 2500 W/m². The lamp was positioned in close proximity to the photothermal tubing to ensure maximal thermal transfer during the regeneration process, thereby enabling a controlled investigation of heat exchange performance.

To assess the influence of flow rate on thermal exchange, the mPES HFMC was operated at two distinct flow rates. Temperature measurements were taken at four key locations: the fiber-side inlet of the HFMC (Point C), the fiber-side outlet (Point D), the shell-side inlet (Point H), and the shell-side outlet (Point I). In an ideal countercurrent heat exchange scenario, the capture solution entering at Point C is initially cool and is expected to be warmed by the counterflowing stream as it exits at Point D. Conversely, the stream entering at Point H, which has just passed through the photothermal regeneration arm and is therefore heated, should gradually transfer its heat to the opposing stream and exit at a lower temperature at Point I.

As the system operates continuously, these temperature values should diverge in a manner indicative of active heat exchange: the temperature at Point D should increase relative to Point C,

and Point I should decrease relative to Point H. Tracking the evolution of these values over time enables quantitative assessment of the HFMC's heat exchange efficiency and the effect of flow rate on system performance.

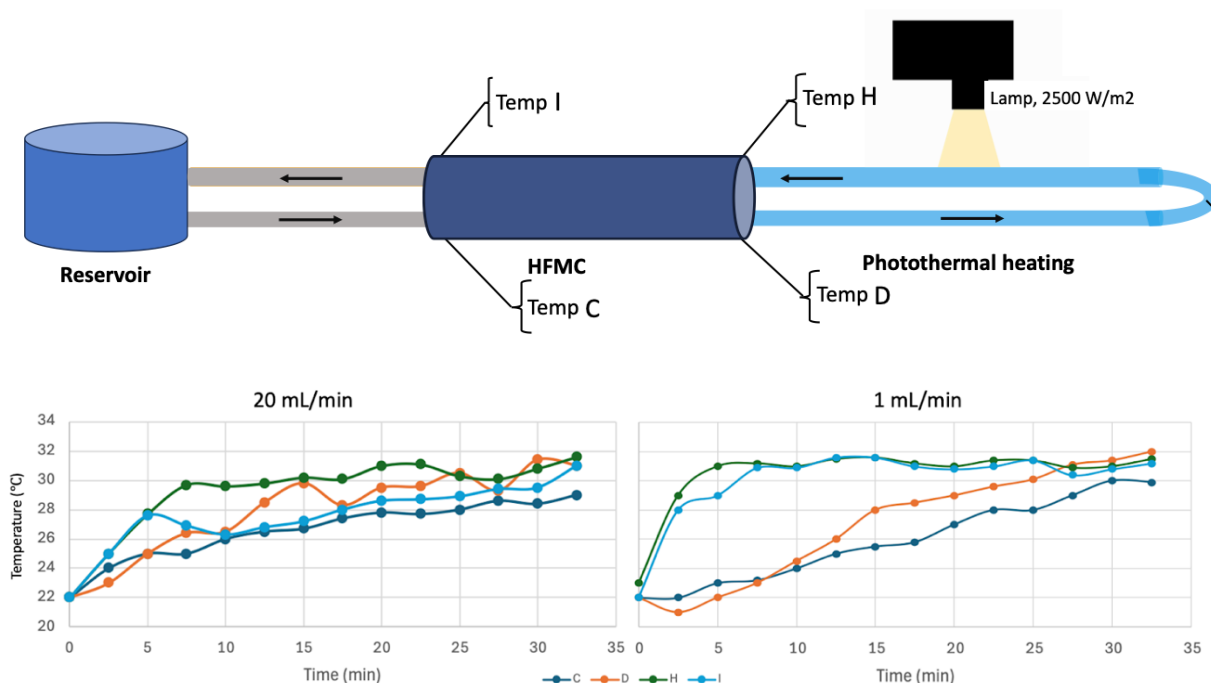


Figure 44 Schematic and results of temperature exchange test for mPES HFMC

The temperature profiles observed during the experiment exhibit an overall upward and converging trend over time, which is consistent with the system continuously cycling and heating the capture solution. However, the convergence of the temperatures toward higher values suggests that complete and sufficient heat exchange is not occurring; specifically, the solution does not return to the desired starting temperature of approximately 25 °C after cycling. This indicates that the current heat exchange configuration is insufficient to fully reset the thermal state of the solution for the next loading cycle.

A clear distinction in performance is observed between the two flow rate conditions tested—20 mL/min and 1 mL/min. At the higher flow rate (20 mL/min), temperatures measured at the four monitoring points (C, D, H, and I) remain relatively similar for the first 10 minutes of operation. Slight divergence begins around the 10-minute mark, with the shell-side input (Point H) registering the highest temperature. At approximately 15 minutes, minor separation appears among the remaining points, suggesting some degree of heat exchange is occurring, albeit limited.

In contrast, at the lower flow rate of 1 mL/min, temperature separation between Points D and H (the outlet of the fiber side and the inlet of the shell side, respectively) and Points C and I (the inlets) occurs much more rapidly—within the first 5 minutes of operation. This indicates more efficient heat transfer under slower flow conditions, likely due to increased residence time in the photothermal arm, which allows more thorough heating by the irradiation source. By the 15-minute mark, temperature separation is clearly observed between Points I and C, while Points H and D begin to converge, suggesting thermal equilibrium is being approached within the HFMC. Eventually, all measured points begin to converge as the system approaches a quasi-steady state.

These initial findings demonstrate that while the HFMC facilitates some level of heat exchange, its current configuration is not optimized to meet the thermal demands of the process. To enhance thermal recovery, several modifications can be considered. First, operating at slower flow rates improves heat transfer and should be further explored. Additionally, increasing the length of the HFMC or the number of hollow fibers would expand the surface area for exchange.

Redesigning the internal geometry of the shell side to include directed flow paths or baffles may improve residence time and mixing, thereby enhancing heat exchange efficiency.

3.4 TEA of HCP Device

Although the Hollow Contactor Photothermal (HCP) device is still under development and has not yet demonstrated full operational functionality, we conducted a preliminary techno-economic assessment (TEA) to evaluate its potential scalability and compare its cost performance to the previously studied Passive Photothermal Capture (PPC) device.

One of the major limitations identified in the TEA of the PPC system was the large volume of capture solution required. Because the PPC system relies on static absorption and desorption within the same physical region, it requires a substantial quantity of sorbent to operate effectively. This not only imposes space and infrastructure constraints but also leads to higher material and capital costs, ultimately challenging its scalability.

In contrast, the HCP system leverages a flow-based configuration in which CO₂ absorption and release occur in separate environments. This decoupling reduces the volume of capture solution needed for regeneration, enabling more compact system designs and potentially lower sorbent costs per unit of CO₂ captured. However, the requirement for active pumping introduces new operational energy demands that must be considered in the overall cost structure.

Despite these additional energy inputs, our initial TEA indicates that the HCP system is more cost-effective to operate than the PPC configuration. A key factor driving this result is the selection of the binding solution. Among those evaluated, potassium glycinate (GLY-K) emerged as the most cost-effective sorbent. Its higher molar CO₂ binding capacity, combined with its low market price, significantly reduced the overall cost of CO₂ capture in the modeled system. Under these assumptions, the projected capture cost approaches a competitive range for direct air capture (DAC) technologies.

Capture Sorbent	OPEX (\$/yr)	\$/tCO₂
MEA	\$ 252,385.77	\$ 272.50
GLY-K	\$ 220,131.45	\$ 237.68
2-DAP	\$ 272,691.45	\$ 294.43
LYS-K	\$ 224,089.51	\$ 242.23

While these early findings are encouraging, it is important to emphasize that they rely on theoretical system performance. Realizing this potential will require successful integration and demonstration of GLY-K in the HCP device, along with further validation of flow stability, CO₂ release efficiency, and long-term sorbent performance.

3.5 Current Design and Future Considerations for HCP Device

3.5.1 Current Design of HCP Device

The design of the HCP device, illustrated in Figure 45, incorporates several key elements that work together to enable efficient CO₂ capture and release, that were previously tested for functionality. At the core of the device is a combination of hollow fiber membrane contactors (HFMCs) that perform distinct functions in the system. The device utilizes an air-liquid HFMC for facilitating contact between the capture fluid and feed gas, a liquid-liquid HFMC for enriching CO₂ concentrations and transferring heat, and another air-liquid HFMC for further CO₂ enrichment and release into the air. Additionally, the design features a photothermal arm for heating, a pump for fluid circulation, and a carefully chosen capture solution to enhance CO₂ uptake.

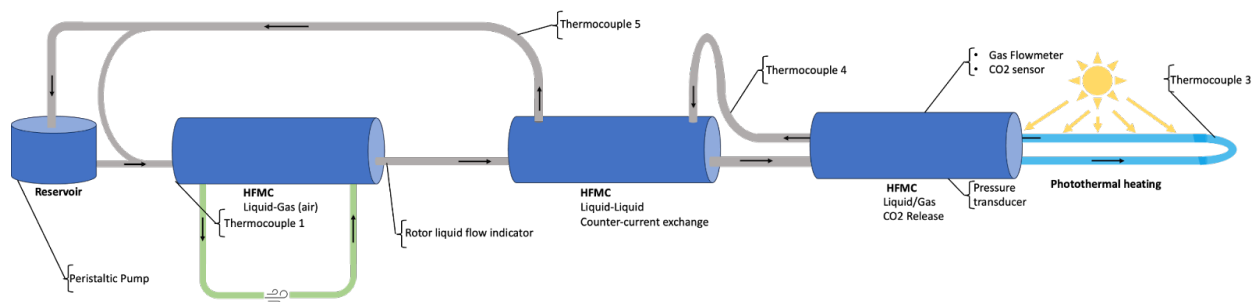


Figure 45 Design of HCP device which incorporates hollow fiber membrane contactors for CO₂ amplification and release, and a glass arm for photothermal heating.

As shown in Figure 45, the HCP device relies on HFMCs for amplifying and releasing CO₂ while employing a glass arm for photothermal heating. The selection and fabrication of HFMCs were determined by availability from manufacturers, ease of in-house production, and compatibility with the chosen capture solution. For air-liquid applications, such as the uptake of CO₂ from the air stream and its subsequent release from the solution, commercially available HFMCs from COBETTER were utilized. These HFMCs feature six modified polyethersulfone

(mPES) fibers, each with an inner diameter of 1.0 mm, housed in a polysulfone casing. In contrast, the liquid-liquid HFMCs, which were used to amplify CO₂ solutes and transfer heat, were fabricated in-house. This process involved using seven expanded polytetrafluoroethylene (EPTFE) fibers, each with a 1.0 mm inner diameter, which were hermetically sealed and integrated into a stainless-steel housing outfitted with ports created through precision machining.

EPTFE was selected as the membrane material for the liquid-liquid HFMCs due to its favorable properties for gas exchange and its compatibility with the aqueous amines employed as the capture solution. Ideally, EPTFE would have been used in all HFMC components of the device, given its superior performance. However, supply limitations and manufacturing constraints necessitated the use of mPES HFMCs provided by COBETTER for the air-liquid contactors. While mPES offers its own advantages, there were initial concerns regarding its compatibility with the selected capture solution. These concerns are addressed in greater detail in the methods section of this work.

The photothermal arm was constructed using two 15 cm borosilicate glass tubes connected via a round plastic tube. This arm was specifically designed to expose the capture solution to sunlight, facilitating photothermal heating and initiating the CO₂ release process.

3.5.2 Current Performance of HCP Device

The HCP device, as currently constructed, integrates all core functional components but has not yet demonstrated the ability to produce statistically significant levels of CO₂ enrichment when

exposed to ambient air. While the system architecture is complete and each sub-component has been tested individually with promising results, the full device does not yet operate at a level sufficient for practical deployment or rigorous quantitative analysis. Continued optimization is required across several aspects of the system.

In the loading arm, carbon dioxide uptake was successfully demonstrated using a hollow fiber membrane contactor (HFMC) fabricated from expanded polytetrafluoroethylene (EPTFE). Operation under lower flow conditions proved critical to achieving measurable loading performance, likely due to the increased residence time and improved mass transfer at reduced flow rates. However, performance decreased at higher flow conditions, indicating the need for further tuning of flow dynamics and membrane contact area. Improvements may be possible through a combination of lower operating flow rates, the use of longer HFMC modules, and further investigation into membrane surface properties that could promote higher gas-liquid contact efficiency.

In the release arm, successful CO₂ desorption was achieved using an HFMC constructed from modified polyethersulfone (mPES), in conjunction with photothermal heating via near-infrared illumination. While desorption was observed under these conditions, extended operation revealed membrane fouling over time, which reduced performance and consistency. In addition, heat exchange within the system remains inadequate. The photothermal arm successfully elevates the temperature of the solution to drive desorption, but the exchanger has not yet been optimized to recover and redistribute thermal energy efficiently. Enhancing heat exchange may be possible through the implementation of longer HFMC modules or by daisy-chaining multiple units to

increase the thermal contact area. Further optimization could also include the use of thermally conductive membrane materials or redesigned flow geometries that promote more effective countercurrent exchange.

Overall, the current state of the HCP device reflects a system in which component-level functionality has been established, but integration and scaling challenges remain. The inability to concentrate CO₂ from ambient air to a statistically significant degree suggests limitations in contact area, membrane performance, and thermal management. Future work should focus on improving the photothermal performance of nanoparticle-enhanced carbon black, treating membrane surfaces to resist fouling and improve gas transfer, and modifying the physical architecture of the device to increase residence time and interfacial area within HFMCs.

4 Conclusions

The work presented in this dissertation contributes to the growing body of research aimed at developing efficient, scalable, and energy-conscious carbon capture technologies. As the climate crisis intensifies, it has become increasingly clear that decarbonization through renewable energy alone will not be sufficient to meet global climate targets. Hard-to-abate sectors such as cement, steel, and heavy transport will continue to emit carbon dioxide for decades to come, necessitating the development of complementary carbon removal strategies. Within this context, this research has pursued a novel pathway: passive photothermal carbon capture systems that harness solar energy to drive CO₂ regeneration without the need for fossil-based thermal input.

This work began by recognizing the dual imperative of advancing carbon capture technologies while addressing the constraints of energy intensity and public acceptability. Conventional point-source capture methods, while relatively efficient in concentrated gas streams, remain costly and heavily dependent on high-temperature regeneration. Direct air capture (DAC), by contrast, is thermodynamically challenging due to the dilute nature of atmospheric CO₂, and its current technological embodiments suffer from high energy demands and material costs. Thus, the central challenge became clear: how to design a system capable of efficiently capturing and regenerating CO₂ from either point sources or ambient air while minimizing thermal and economic burdens.

To this end, a photothermal capture strategy was pursued, with initial studies focused on the development of a Passive Photothermal Capture (PPC) device. This device utilized a nanosolution of oxidized nanocarbon black (NCB) suspended in an amine-based capture liquid to harness sunlight for CO₂ desorption. The photothermal approach allowed for a bulk regeneration temperature decrease of up to 50°C compared to conventional heating, offering a promising avenue for low-grade thermal regeneration. The PPC system, using a blend of monoethanolamine, dimethylacetamide, and water, achieved a maximum regeneration efficiency of 4.4 mol CO₂ per MJ—comparable to other commercially available methods—highlighting its viability in concentrated CO₂ environments.

However, the PPC device's performance declined significantly when applied to ambient air conditions, where CO₂ concentrations are approximately 400 ppm. This limitation prompted the design and fabrication of a second-generation system: the High Contact Photothermal (HCP) Device. The HCP system addressed the diffusion and residence-time limitations inherent in the

PPC device by incorporating hollow fiber membrane contactors (HFMCs) for gas-liquid and liquid-liquid mass transfer, coupled with a flow-based architecture and photothermal heating arm. Through careful selection of membrane materials—including ePTFE for gas exchange compatibility—and iterative design improvements, the HCP system demonstrated the potential to enhance CO₂ uptake and regeneration across a multi-step fluidic pathway.

Despite these advancements, the fully integrated HCP Device has not yet achieved statistically significant enrichment of CO₂ from ambient air. Experimental results showed that while individual subcomponents function effectively—particularly in isolated membrane modules or regeneration arms—the complete system requires further optimization to achieve the desired separation performance. Specific challenges remain in improving contact efficiency within the loading arm, mitigating membrane fouling, enhancing photothermal heat transfer, and maintaining consistent fluid dynamics within the capture loop.

Alternative sorbents were evaluated to improve system performance under ambient conditions. Potassium glycinate (K-GLY) and diglycolamine (DGA) emerged as superior candidates compared to traditional MEA and MMEA solutions, offering both improved thermal stability and lower regeneration temperatures under photothermal conditions. The incorporation of K-GLY allowed a favorable trade-off between cost, availability, and molar CO₂ capacity, which was further corroborated by a preliminary techno-economic analysis. This analysis suggested that the HCP device configuration could be more cost-effective to operate at scale than its PPC predecessor, provided that critical integration challenges are addressed.

This research demonstrates that passive photothermal systems, when coupled with advanced membrane contactor designs, present a potential direction for the development of energy-efficient carbon capture technologies. While significant hurdles remain in scaling and optimizing the HCP architecture, the foundational work laid out in this dissertation offers a clear roadmap for future improvements. Continued research should focus on enhancing photothermal material performance, refining membrane geometry and surface properties to reduce fouling and increase gas flux, and redesigning system architecture to maximize interfacial area and residence time.

The broader implications of this work extend beyond the technical challenges of carbon capture. By reducing energy inputs and eliminating the need for fossil-derived regeneration heat, photothermal systems could lower the lifecycle carbon footprint and economic barriers associated with carbon removal technologies. As governments, industries, and scientists seek viable solutions to achieve net-zero emissions, innovations such as those described here will be essential in closing the gap between ambition and action. This thesis stands as a testament to the potential of interdisciplinary innovation—spanning chemistry, materials science, and engineering—to contribute meaningfully to the global fight against climate change.

Bibliography

1. *AR6 Synthesis Report: Climate Change 2023*. **IPCC**. 2023.
2. *Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. **IPCC**. 2022, Cambridge University Press.
3. *IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. **Romero, H. Lee and J.** 2023.
4. *Direct Capture of CO₂ from Ambient Air*. **Sanz-Pérez, E. S., Murdock, C. R., Didas, S. A., & Jones, C. W.** 2016, Chemical Reviews.
5. *Assessing the Economics of CO₂ Capture in China's Iron/Steel Sector: A Case Study*. **Xi, Liang & Lin, Qianguo & Muslemani, Hasan & Ming, Lei & Qiang, Liu & Jia, Li & Alisa, Wu & Muxin, Liu & Francisco.** 2019, Energy Procedia, pp. 3715-3722.
6. *Carbon Capture*. **Wilcox, J.** 2012, Springer.
7. *Amine Scrubbing for CO₂ Capture*. **Rochelle, G. T.** 2009, Science, pp. 1652–1654.
8. *Reducing the Cost of CO₂ Capture from Flue Gases Using Aqueous Chemical Absorption*. **Wiley, Anggit Raksajati Minh T. Ho Dianne E.** 2013, Industrial & Engineering Chemistry Research, pp. 16887–16901.
9. *Development of novel AMP-based absorbents for efficient CO₂ capture with low energy consumption through modifying the electrostatic potential*. **Lu, G, Wang, Z, Yue, Z, Wei, W, Huang, Y, Zhang, X & Fan, X.** 2023, Chemical Engineering Journal.

10. **Argonne National Laboratory.** Transportation and Power Systems: Carbon Capture.
[Online] 2024. <https://www.anl.gov/taps/carbon-capture#:~:text=Point%20Source%20is%20the%20lowest,energy%20consumption%20of%20Point%20Source.>
11. *A Unified Approach to CO₂–Amine Reaction Mechanisms.* **Ridha Ben Said, Joel Motaka Kolle, Khaled Essalah, Bahoueddine Tangour, and Abdelhamid Sayari.** 2020, ACS Omega , pp. 26125-26133.
12. *Advancements in CO₂ capture by absorption and adsorption: A comprehensive review.* **Xiang Yun Debbie Soo, Johnathan Joo Cheng Lee, Wen-Ya Wu, Longgang Tao, Cun Wang, Qiang Zhu, Jie Bu.** 204, Journal of CO₂ Utilization.
13. *A review on progress made in direct air capture of CO₂.* **Sodiq, Ahmed & Abdullatif, Yasser & Aïssa, Brahim & Ostovar, Arash & Nassar, Nashaat & El-Naas, Muftah & Amhamed, Abdukarem.** 2022, Environmental Technology & Innovation.
14. **Neg8Carbon.** <https://neg8carbon.com/dac-technologies/>. [Online] 2024.
15. **Romm, Joseph.** *Why direct air carbon capture and storage (DACCS) is not scalable and ‘net zero’ is a dangerous myth.* s.l. : Penn Center for Science, Sustainability, and the Media, 2024.
16. **Douglas, Leah.** *US carbon capture pipeline setbacks reflect challenges in climate fight.* s.l. : Reuters, 2023.
17. **Beach, Jeff.** *North Dakota approves CO₂ storage for Summit pipeline.* s.l. : Iowa Capital Dispatch, 2024.
18. **Brown, Parker.** *Lake County Commission rejects petition for pipeline ordinance.* s.l. : Dakota News, 2025.

19. **Douglas, Leah.** *Navigator CO2 Ventures cancels carbon-capture pipeline project in US Midwest.* s.l. : Reuters, 2023.
20. **Summit Carbon Solutions.** Project Footprint. *Project Footprint.* [Online] 2023.
<https://summitcarbonsolutions.com/project-footprint/>.
21. **Smith, Erin E.** *The Cost of CO2 Transport and Storage in Global Integrated Assessment Modeling b.* s.l. : University of California, Berkeley, 2015.
22. **Brown, Jenn.** Institute for Responsible Carbon Removal. [Online] 2021.
<https://research.american.edu/carbonremoval/2021/11/10/co2-pipelines-navigating-the-complexities-and-nuances-through-expert-opinions/#:~:text=We%20transport%20it%20as%20a,than%20other%20types%20of%20pipelines..>
23. **Magnus Killingland, Matias Boge.** *Potential for reduced costs for carbon capture, transport and storage value chains (CCS).* s.l. : DNV, 2020.
24. *The impact of climate on solvent-based direct air capture systems.* **Keju An, Azharuddin Farooqui, Sean T. McCoy,.** s.l. : Applied Energy, 2022, Applied Energy.
25. **Meckel, Alex Bump, Susan Hovorka.** *The US Gulf Coast is poised for rapid methane and CCS development.* s.l. : Gulf Coast Carbon Center, Bureau of Economic Geology, 2021.
26. *Techno-Economic Assessment Guidelines for CO2 Utilization.* **Zimmermann Arno W., Wunderlich Johannes , Müller Leonard , Buchner Georg A. , Marxen Annika , Michailos Stavros , Armstrong Katy , Naims Henriette , McCord Stephen , Styring Peter , Sick Volker , Schomäcker Reinhard.** s.l. : Frontiers in Energy Research, 2020, Frontiers in Energy Research.

27. **Shell Catalysts & Technologies.** Quest Facility Spotlight: showing how large-scale CO₂ capture can be safe and effective. *shell.com*. [Online] 2021.
28. **Lockwood, Toby.** *Carbon capture and storage: What can we learn from the project track record?* s.l. : Clean Air Task Force, 2024.
29. **Aker Solutions.** Carbon Capture. [Online] 2025. <https://www.akersolutions.com/who-we-are/power-the-change/carbon-capture/>.
30. *Current status and pillars of direct air capture technologies.* **Mihrimah Ozkan, Saswat Priyadarshi Nayak, Anthony D. Ruiz, Wenmei Jian.** 2022, iScience.
31. *A review of direct air capture (DAC): scaling up commercial technologies and innovating for the future.* **McQueen, Katherine Vaz Gomes, Colin McCormick, Katherine Blumanthal, Maxwell Pisciotta, Jennifer Wilcox.** 2021, Progress in Energy.
32. *Engineered carbon mineralization in ultramafic rocks for CO₂ removal from air: Review and new insights.* **Peter B Kelemen, Noah McQueen, Jennifer Wilcox, Phil Renforth, Greg Dipple, Amelia Paukert Vankeuren.** 2020, Chemical Geology.
33. *The cost of direct air capture and storage can be reduced via strategic deployment but is unlikely to fall below stated cost targets.* **John Young, Noah McQueen, Charithea Charalambous, Spyros Foteinis, Olivia Hawrot, Manuel Ojeda, Hélène Pilorgé, John Andresen, Peter Psarras, Phil Renforth, Susana Garcia, Mijndert van der Spek,.** 2023, One Earth.
34. *Total cost of carbon capture and storage implemented at a regional scale: northeastern and midwestern United States.* **William J. Schmelz, Gal Hochman and Kenneth G. Miller.** 2020, Royal Society Interface Focus.

35. *Carbon capture utilization and storage in review: Sociotechnical implications for a carbon reliant world.* **Hope McLaughlin, Anna A. Littlefield, Maia Menefee, Austin Kinzer, Tobias Hull, Benjamin K. Sovacool, Morgan D. Bazilian, Jinsoo Kim, Steven Griffiths.** 2023, Renewable and Sustainable Energy Reviews.
36. *Comparative Review for Enhancing CO₂ Capture Efficiency with Mixed Amine Systems and Catalysts.* **Jiang, Lin Y, Sun C, Sun Y, Zhu Y.** 2024, Molecules.
37. *MEA-based CO₂ capture: a study focuses on MEA concentrations and process parameters.* **Nan, Wang Dong , Krook-Riekkola Anna , Ji Xiaoyan.** 2023, Frontiers in Energy Research.
38. *Solvent Effects on the Photothermal Regeneration of CO₂ in Monoethanolamine Nanofluids.* **Nguyen, Stolaroff J, Esser-Kahn A.** 2015, ACS Appl Mater Interfaces.
39. **Rao, Edward S. Rubin and Anand B.** *A Technical, Economic and Environmental Assessment of Amine-based CO₂ Capture Technology for Power Plant Greenhouse Gas Control.* s.l. : U.S. Department of Energy National Energy Technology Laboratory, 2002.
40. *Mechanisms of CO₂ Capture into Monoethanolamine Solution with Different CO₂ Loading during the Absorption/Desorption Processes.* **Lv, Guo B, Zhou Z, Jing G.** 2015, Environ Sci Technol.
41. *CO₂ Capture and Release in Amine Solutions: To What Extent Can Molecular Simulations Help Understand the Trends?* **Ma C, Pietrucci F, Andreoni W.** 2023, Molecules.
42. *A SELECTION OF AMINE SORBENTS FOR CO₂ CAPTURE FROM FLUE GASES.* **Wilk, Lucyna Więclaw-Solny¹, Dariusz Śpiewak , Tomasz Spietz, Hanna Kierzkowska-Pawlak.** 2015, Proc. Eng.
43. *Evaluating CO₂ Capture Performance of Trisolvent MEA–BEA–AMP with Heterogeneous Catalysts in a Novel Bench-Scale Pilot Plant.* **Zhang, Huancong Shi, Hanyun Wang,**

Yongcheng Feng, Jing Jin, Paitoon Tontiwachwuthikul, and Mengxiang Fang. 2024, ACS Omega.

44. *Photothermal release of CO₂ from capture solutions using nanoparticles.* **Nguyen, Richard Truong, Richard Lee, Samantha Goetz, Aaron EsserKahn.** 2014, Energy and Environmental Science.

45. *A Unified Approach to CO₂–Amine Reaction Mechanisms.* **Said, Joel Motaka Kolle, Khaled Essalah, Bahoueddine Tangour, and Abdelhamid Sayari.** 2020, ACS Omega.

46. *Catalysts and inhibitors for oxidative degradation of monoethanolamine.* **Sexton, Andrew and Rochell, Gary.** 2009, International Journal of Greenhouse Gas Control, pp. 704-711.

47. *Monoethanolamine Degradation Rates in Post-combustion CO₂ Capture Plants with the Capture of 100% of the Added CO₂*
Monoethanolamine Degradation Rates in Post-combustion CO₂ Capture Plants with the Capture of 100% of the Added CO₂. **Daniel Mullen, Lucas Braakhuis, Hanna Katariina Knuutila, Jon Gibbins, and Mathieu Lucquiaud.** 2024, Industrial & Engineering Chemistry Research, pp. 13677-13691.

48. *Review of carbon capture absorbents for CO₂ utilization.* **Chai, Lock Hei Ngu and Bing Shen How,.** 2022, Greenhouse Gases Science and Technology, pp. 12:394-427.

49. *Cost-effective solar-driven configurations for post-combustion carbon capture at Abadan Power Plant: MEA, DEA, and DGA absorption-based,.* **Hosseinifard, Milad Hosseinpour, Mohsen Salimi, Majid Amidpour,.** 2024, Cleaner Engineering and Technology.

50. **Koech P.K., D. Barpaga, D. Malhotra, A. Kumar, and A. Zwoster.** *Assessment of Amine-Based CO₂BOLs for Direct Air Capture.* s.l. : Pacific Northwest National Laboratory., 2024.

51. *A single-component water-lean post-combustion CO₂ capture solvent with exceptionally low operational heat and total costs of capture – comprehensive experimental and theoretical*

evaluation. **Heldebrant, Richard Zheng, Dushyant Barpaga.** 2020, Energy & Environmental Science.

52. *Thermal modulation of reaction equilibria controls mass transfer in CO₂-binding organic liquids.* **Moore, Anthony J. Varni, Simon H. Pang, Sneha A. Akhade, Sichi Li, Du T.**

Nguyena and Joshua K. Stolarof. 2023, Energy & Environmental Science.

53. *Direct Air Capture of CO₂ with Aqueous Amino Acids and Solid Bis-iminoguanidines (BIGs).*

Custelcean, R., et al. 2025, ACS Sustainable Chemistry & Engineering.

54. *Reactive capture of CO₂ via amino acid.* **Xiao, Y.C., Sun, S.S., Zhao.,** 2024, Nat Commun .

55. *Reaction kinetics of carbon dioxide with aqueous solutions of l-Arginine, Glycine & Sarcosine using the stopped flow technique.* **Mahmud, Abdelbaki Benamor, Mustafa S.**

Nasser, Mohammed J. Al-Marri, Hazim Qiblawey, Paitoon Tontiwachwuthikul. 2017,

International Journal of Greenhouse Gas Control.

56. *CO₂ absorption using aqueous potassium lysinate solutions: Vapor - liquid equilibrium data and modelling.* **Shen, Shufeng and Zhao, Yue and Bian, Yangyan.** 2017, Journal of Chemical Thermodynamics.

57. *Kinetics of CO₂ Absorption into Aqueous Basic Amino Acid Salt: Potassium Salt of Lysine Solution.* **Shen S, Yang YN, Bian Y, Zhao Y.** 2016, Environ Sci Technol, pp. 50(4):2054-63.

58. **National Energy Technology Laboratory.** *Membranes for Carbon Capture.* s.l. : U.

59. *Sub-Ambient Temperature Direct Air Capture of CO₂ using Amine-Impregnated Metal–Organic Frameworks.* **Kim, E. J., et al.** 2022, JACS Au, pp. 404-416.

60. *Enhanced Tolerance to Flue Gas Contaminants on Carbon Dioxide Capture Using Amine-Functionalized Multiwalled Carbon Nanotubes.* **Wang, J., et al.** 2014, Energy & Fuels, pp. 6494–6501.

61. *New absorption liquids for the removal of CO₂ from dilute gas streams using membrane contactors.* **Kumar, J. A. Hogendoorn, P. H. M. Feron, G. F. Versteeg.** 2002, Chemical Engineering Science.
62. *A study of mass transfer resistance in membrane gas–liquid contacting processes.* **M. Mavroudi, S.P. Kaldis, G.P. Sakellarpoulos.** 2006, Journal of Membrane Science.
63. *Hollow fiber membrane contactor for CO₂ capture: A review of recent progress on membrane materials, operational challenges, scale-up and economics.* **Shiravi, Mohammad Salehi Maleh, Ahmadreza Raisi, Mika Sillanpää.** 2024, Carbon Capture Science & Technology.
64. *Analysis of Laplace–Young equation parameters and their influence on efficient CO₂ capture in membrane contactors.* **Bougie, Maria C. Iliuta,.** 2013, Separation and Purification Technology, pp. 806-815.
65. *Gas-liquid membrane contactors for carbon dioxide separation: A review.* **Seungju Kim, Colin A. Scholes, Daniel E. Heath, Sandra E. Kentish.** 2021, Chemical Engineering Journal, pp. 1385-8947.
66. *Stability of Porous Polymeric Membranes in Amine Solvents for Membrane Contactor Applications.* **Kalmykov D, Shirokikh S, Grushevenko EA, Legkov SA, Bondarenko GN, Anokhina TS, Molchanov S, Bazhenov SD.** 2023, Membranes (Basel).
67. *An effective air–liquid contactor for CO₂ direct air capture using aqueous solvents.* **Kasturi, Abishek, et al.** 2023, Separation and Purification Technology.
68. —. **Tsouris, Costas et. al.** 2023, Separation and Purification Technology.
69. *A Review on Hollow Fiber Membrane Contactors for Carbon Capture: Recent Advances and Future Challenges.* **Ramezani, R. et al.** 2022, Processes, p. 10(10).

70. *Solvent Effects on the Photothermal Regeneration of CO₂ in Monoethanolamine Nanofluids*. **Nguyen D, Stolaroff J, Esser-Kahn A.** 2015, ACS Appl Mater Interfaces, pp. 7(46):25851-6.
71. **Environmental Protection Agency.** epa.gov/ghgemissions. [Online]
72. *Gas-Liquid Hollow Fiber Membrane Contactors for Different Applications*. **Bazhenov, S. et al.** 2018, Fibers.