Biologically-mediated carbon capture and utilization by microalgae towards sustainable CO_2 biofixation and biomass valorization – A review

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ABSTRACT

The continuously rising emission of carbon dioxide (CO_2) is a universal hazard which urgently requires collaborative action between policymakers and scientists. International treaties such as the Paris Agreement (with 196 signatories) reflect the importance of anthropogenic climate change as a truly global public concern. Towards the aim of climate recovery, the most broadly utilized CO_2 reduction strategies, including carbon capture and storage (CCS); carbon capture, utilization, and storage (CCUS); and carbon capture and utilization (CCU) are reviewed herein. Of these methods, CCU shows the greatest potential by recycling captured CO_2 and harnessing it as a resource to generate emissions-neutral or -negative value-added products (VAPs). Within CCU methodologies, biologically-mediated CCU (bio-CCU) by microalgae is a promising biotechnology to drastically reduce CO_2 emissions. This review therefore details the mechanisms of photosynthesis to sequester CO_2 and incorporate it into valuable biomolecules. Microalgal cells utilize CO_2 as precursors of macromolecules, including lipids, proteins, carbohydrates, and pigments; all of which are discussed within the frame of industrial relevance and market value. The biofixation potential of microalgae is clearly demonstrated by the carbon content of the myriad VAPs they produce. Moreover, pathways towards decreasing carbon footprint (via carbon capture prior to emission to the atmosphere) and increasing carbon handprint (reducing carbon emissions by consuming CO_2-neutral or -negative products) related to bio-CCU are presented herein. Finally, existing challenges and knowledge gaps are acknowledged and described, and future research needs are recommended.

1. Introduction

The battle against catastrophic climate change has never been hotter, as the year 2020 concluded as one of the hottest years in recorded history [1]. In December 2018, the atmospheric concentration of CO_2 at the Mauna Loa scientific recording station (Hawaii, USA) was measured at 409.23 ppm; the highest CO_2 concentration recorded in at least 3 million years [2]. Extreme weather events caused by climate change are taking a serious toll on human lives and livelihoods, while climate-related loss of terrestrial, aquatic, and marine biodiversity is compounding this suffering across the planet. In many cases, economic disparities are growing, as climate change can drastically diminish productivity on land, as well as within freshwater and marine ecosystems. There is growing evidence that current geopolitical conflicts are being driven by extreme weather events, food insecurity, economic

disruption, and persistent drought; all of which trigger mass human migration, and all of which are intricately linked with a changing climate [3].

The physical science of climate change drivers is well studied and broadly understood [4]. Excessive emission of greenhouse gases (GHGs), most notably carbon dioxide (CO_2), but including other gases (e.g. methane (CH_4) and nitrous oxide (N_2O)), and non-gases (e.g. aerosols and particulates like black carbon) results in accumulation of these compounds in the atmosphere. These gases and compounds cause a physical effect known as radiative forcing (RF) which is the primary driver of climate change [4]. RF occurs when these compounds absorb outgoing infrared energy, instead of allowing it to escape earth's atmosphere into space. This absorbed energy is redirected, either upwards or downwards. When an atmospheric component redirects infrared radiation downwards (back to earth), its

radiative forcing potential is positive (measured in W m^2) [5].

As it is by far the most abundantly emitted GHG by mass, CO_2 is responsible for the majority of climate-warming radiative forcing, and, as such, it is the target of most climate mitigation efforts. Apart from the net effect of climate warming, however, CO_2 is responsible for another severely detrimental geochemical process affecting the entire planet: ocean acidification. The chemistry of ocean acidification is relatively simple; CO_2 is soluble in alkaline seawater (the global average surface pH of the world's oceans is 8.1), and so the ocean takes up approximately 25% of anthropogenic CO_2 emissions from the atmosphere [6]. Dissolving CO_2 in water generates carbonic acid (H_2CO_3), which rapidly dissociates into carbonate ions (CO_3^{2-}) and hydrogen ions (H^+) [6]. Increasing the H^+ concentration of any liquid decreases its pH, and this has significant implications for marine life and the role that they play in global biogeochemical cycles.

Worrisome data published by the International Energy Agency (IEA) in March 2021 indicates that despite a global emission decline of nearly 2 billion tonnes in 2020, CO_2 emissions are once again on the rise [7]. Compared with December 2019, global energy-related CO_2 emissions were 2% higher in December 2020 as economies struggle to bounce back after a year of COVID-caused contraction [7]. In many cases, the return to "business as usual" emissions is setting countries farther back on already-lagging emissions reduction targets, pledged by 196 nations party to the 2015 Paris Agreement. This unwelcome development comes just ahead of the United Nations Framework Convention on Climate Change (UNFCCC) 26th Conference of the Parties (COP26), to review progress made towards Paris targets and agree a path to carbon-neutrality in the foreseeable future.

The Paris Agreement is not the first multilateral treaty of this type; the Montreal Protocol on Substances that Deplete the Ozone Layer is widely considered to be the most successful multilateral agreement on environmental action in human history. It remains the only United Nations treaty to be ratified by all 198 member states. Equally important as its political success, the Montreal Protocol has been a scientific triumph. By phasing out almost 100 ozone-depleting substances (many of which are potent GHGs) in an economically feasible way, the infamous hole in the ozone layer is projected to close completely by 2050. Unfortunately, some of the most abundant and effective GHGs (e.g. CO_2 and CH_4) are not regulated by Montreal, and no further multilateral agreements on environmental or climate action have had such astounding success. The Kyoto Protocol set more ambitious, binding emissions reduction targets; however, although it was a political victory, the Kyoto Protocol did not achieve the same real-world effect as Montreal. In almost every case of international law, there is a tradeoff of political success for scientific success, or vice versa; if policies are too strict, member states choose not to sign or ratify the agreement, and if policies are not strict enough, significant change is not achieved, no matter how many signatories ratify it. In an era of unprecedented civilian access to international news and policymaking, governments are under pressure like never before to uphold their Paris climate pledges. In 2020, all 196 parties submitted their nationally determined contributions and implementation strategies to achieve the goals laid out in the Paris Agreement. Due to this climate-neutral momentum, the UN reports that by 2030, zero-carbon technologies could prove to be economically competitive in sectors which historically represent more than 70% of global emissions. With these legal foundations taking shape, research and technological development must keep a swift pace, and synchronize with economic trends. This challenge presents an unprecedented opportunity to safeguard our future with economically-sound carbon capture and utilization (CCU) technologies; to this end, the present review outlines conventional practices and establishes sustainable CO_2 biofixation by microalgae as the most promising CCU technique (bio-CCU). The novelty of the microalgal bio-CCU approach lies in its simplicity and its potential for cost-efficacy; it can be adopted across a spectrum of climate zones, economic categories, and technological capacities. Universal applicability is the key to finding universal solutions. This review concludes that the global economy must reinvent itself such that the carbon handprints of manufactured goods exceed industrial carbon footprints.

2. The economic advantages of controlling CO_2 emissions

Carbon emissions are deeply embedded in the global economy. Every sector pollutes, but the most notoriously carbon-intensive sectors are energy and transport. A 2019 report published by the National Energy Technology Laboratory (NTEL, USA) recommended a carbon capture cost target maximum of $40/tonne CO_2; however, even the most well-established CO_2 capture methods far exceed this cost margin [8]. Another recently published analysis of global efforts to meet the ambitious 2° C Paris Agreement target found that, while technically and economically feasible, the costs of meeting this goal require steadfast global collaboration [9]. Wei et al. [9] proposed a global layout for cost-effective carbon capture and utilization (CCUS), considering a global average CO_2 price of approximately $62.65/tonne CO_2. The strategy they define requires nearly $8.20 trillion of financial investment, which, even when offset with traditional carbon capture (enhanced oil recovery, EOR) benefits, results in a total cost of $5.76 trillion through the year 2050 [9]. This extraordinary cost can technically be met by collaborative intergovernmental efforts. Commercial success is much more achievable if these costs can be lowered by adopting novel cost-saving techniques, such as bio-CCU, on the industrial scale.

In an attempt to decarbonize energy, transport, and other sectors without severe disruption, carbon taxation and trading have evolved as legislative mechanisms, creating new and sustainable climate-forward markets. The largest carbon trading market in the world is the EU's Emissions Trading System, or ETS [10]. At its inception in 2005, the ETS established an emissions cap that currently affects more than 11,000 energy-intensive industrial installations. Companies receive or purchase emission allowances which they can trade with other companies under the ETS scheme (commonly known as "cap and trade"). Additionally, international credits are granted by taking part in emission-saving projects worldwide. The ETS framework is organized into four phases. Phases 1–2 took place during 2005–2012, and Phase 3 was recently concluded at the end of 2020. A primary goal of Phase 4, which entered into force on 1 January 2021, is to increase international competitiveness, and to provide strong economic incentives for companies to make technological progress in innovative negative emissions technologies by continuing to allocate free allowances and funding for such endeavors [10].

The European Commission and Council has agreed several reform amendments to the ETS directive which have specific consequences for implementing Phase 4. One such amendment reduced the overall emissions cap from 1.74% (2013–2020) to 2.2% each year from 2021 to 2030, thereby reducing EU CO_2 emissions in the ETS-affected sectors by 43% as compared to 2005. Another amendment created a 12% "automatic set-aside" reserve mechanism of verified annual emissions (a reserve of at least a 100 million CO_2 permits) from 2021 to 2030; essentially, a carbon cost floor with a price range set each year by the European Commission's Directorate General for Climate Change [11]. While carbon allowances still exist, auctioning is now the dominant method of carbon trading; this translates to far fewer "free" emissions allowances, and restrictions will continue to tighten.

Inspired by the success of the EU ETS, in terms of both economics and progress towards Paris Agreement pledges, many other economies across the planet have adopted similar carbon trading schemes. The economic inertia of global carbon markets must be matched with technological advances, such that companies can remain competitive as carbon trading continues to evolve.

Carbon trading and taxation is one way to view the economics of emissions reduction, but another major consideration is the expense incurred by climate-related disasters. The effects of climate change are causing catastrophic extreme weather events; a recent example can be

found in Texas (USA), where unprecedented ice and snow has caused extensive damage to energy grids and water infrastructure, as well as tragic loss of life [12]. Another more indirect example is the oil spill incident in February 2021 which devastated Israel's Mediterranean coast. Throughout human history, climatic change has driven mass migrations, which almost always result in deadly conflict. Mitigating these disasters is astronomically expensive; even the most conservative estimates of the global cost of climate change are staggering.

Finally, to provide some cost/benefit perspective on the value of carbon capture to mitigate climate change, an article published in October 2020 compared pledged COVID mitigation funding to current estimates of funds needed to adhere to Paris commitments. This study determined that investing a meager 12% of pledged COVID-19 stimulus funding (per year through 2024) in low-carbon, fossil-free energy projects would result in meeting the Paris Agreement's most ambitious target and limit net global warming to 1.5°C [13]. This article does not take into account the potential economic gains that can be made by structuring these investments such that carbon emissions are captured (rather than simply limited), and upgraded into saleable value-added products alongside emissions-neutral or -negative energy.

Carbon capture generates wealth in three ways: 1) economic incentives within existing carbon markets, 2) preventing costly environmental and humanitarian disasters resulting from uncontrolled climate change, and 3) upgrading a damaging waste product into valuable products and renewable energy. The physical science and practical implementation of these three themes are discussed in detail in this review.

3. Limiting CO_2 emissions

Considering the aforementioned legislative, economic, and environmental incentives to limit carbon emissions, three major strategies of CO_2 sequestration have evolved, namely; oxy-fuel combustion capture, pre-combustion capture, and post-combustion capture, in accordance with the existing facilities of modern power plants [14]. Capturing CO_2 emitted by the combustion of carbon-based fuels (mainly fossil-based) by these strategies is performed using different oxygen concentrations, pressures, and combustion temperatures; all of which significantly affect the amount of exhausted CO_2 from the power plant.

Generally, the flue gas generated from burning fossil fuels in atmospheric air contains high concentrations of N_2 (70%), lower concentrations of CO_2 (15%), and minor components of H_2O, NO_x, CO, and SO_x [15]. Oxy-fuel combustion has been developed to reduce the concentration of N_2 in the flue gas. For this purpose, fuel is combusted in the presence of nearly pure oxygen instead of air. Depending on the type of fuel used, the combustion in an N_2-free environment produces a flue gas with high CO_2 concentration (80–98%), particulate matter, SO_2, and water vapor. Particulate matter and SO_2 are separated from the steam of oxy-fuel via electrostatic precipitation and flue gas desulfurization (FGD), respectively [16]. Then, high CO_2 concentrations are easily purified using the low-energy process of water vapor condensation.

Another advantage of oxy-fuel combustion is the lower volume of flue gas produced due to suppression of N_2 and NO_x production. It requires smaller equipment for flue gas treatment, which ultimately reduces the operational cost and energy requirements. It should be noted that the oxy-fuel combustion system requires additional equipment, such as air separation units (for oxygen generation), flue gas circulation systems, and CO_2 condenser/compressors to be compatible with traditional air combustion systems [17]. High energy consumption (200 kWh/tonne O_2) by the air separation unit to produce a large amount of pure oxygen is considered the most significant disadvantage of oxy-fuel combustion [16]. Fig. 1 shows the schematic diagram of CO_2 capture from oxy-fuel combustion.

Pre-combustion is another carbon capture strategy that removes carbon from fuel before complete combustion. In pre-combustion, initially, natural gas or coal is pre-treated using reactions such as steam reforming and gasification before it is combusted. Pre-treatment is conducted in the presence of air, oxygen, or steam to convert the fuel to syngas, which is a mixture of CO and H_2. The pre-combustion process is followed by a water–gas shift reaction to pass syngas through a catalytic reactor under high pressure (5–40 bar), where CO is converted to CO_2 (20–40%), and additional H_2 (40–60%) is produced [15,18]. Higher concentrations of CO_2 (>20%) compared to post-combustion (<15%) facilitates separation from H_2. Additionally, the H_2 produced can be used in thermal power plants or other industries as a source of green energy. Despite these advantages, however, the high temperature of H_2-rich turbine fuel is a major drawback of pre-combustion carbon capture, as it requires cooling prior to separation. Moreover, the fundamental modifications required to existing flue gas systems increase the total capital costs of this method [15,16,18].

Among CO_2 capture strategies, post-combustion capture is the simplest and most widely used method that can be retrofitted to extant power plants with minimal infrastructure change [19]. Post-combustion capture refers to CO_2 recovery before flue gas is emitted to the atmosphere. As this pathway burns fuel in air, it requires CO_2 separation from flue gas with very high concentrations of N_2 (70%). This separation step can be energy intensive, as CO_2 concentrations in flue gas are less than 15% (10–15% in coal-fired and 4–7% in gas-fired) [20].

Additionally, once captured, CO_2 requires purification (to concentrations above 95%) to be acceptable quality for compression, transportation, and storage processes [15,18]. Therefore, efficient carbon capture methods are needed to remove CO_2 from high volumes of flue gas with low CO_2 concentrations. The next section introduces absorption, adsorption, and membrane separation as well-known CO_2 capture methods and discusses their efficacy.

4. Conventional CO_2 capture methods

4.1. Absorption

In CO_2 absorption methods, a gas mixture containing CO_2 is reacted with a solvent to dissolve gaseous CO_2 in a liquid phase. Depending on
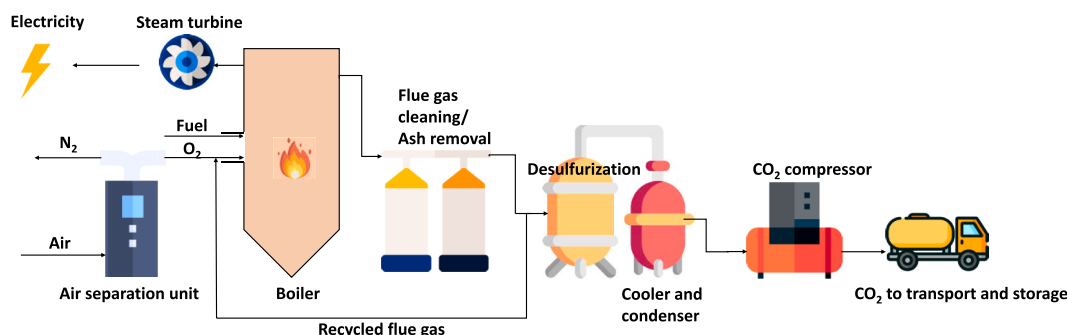

Fig. 1. Oxy-fuel combustion system (adapted from Seddighi et al. [144]).

the nature of the solvent, absorption can be divided into physical and chemical processes. In chemical absorption, solvents form strong chemical bonds with CO_2 under atmospheric conditions. Due to this ability, chemical absorption has been used as an efficient method for the removal of CO_2 with low partial pressure in post-combustion carbon capture [21]. This method is the first technology that has been commercialized on an industrial scale [22]. Currently, amine-based alkali solvents such as monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and di-2-propanolamine (DIPA) are considered to be the most promising compounds for chemical absorption of CO_2 in thermoelectric power plants [16]. Because of its high CO_2 absorption efficiency (>90%), monoethanolamine (MEA) was the first amine-based solvent applied for this purpose, and is therefore one of the most mature technologies for post-combustion CO_2 capture [16]. Lv et al. [23] investigated the mechanisms of chemical absorption and desorption of CO_2 in MEA solution under variable CO_2 loading (Fig. 2). They stated that the reaction begins with the fast, exothermic reaction between MEA and CO_2, and forms carbamate under low CO_2 load. The reaction is followed by the hydration of CO_2 to bicarbonate (HCO_3^-)/carbonate (CO_3^{2-}) under high CO_2 load. These species are also transferred to carbamate via reaction with MEA; this reaction is accompanied by carbamate hydrolysis. Subsequently, CO_2 is released from carbamate through thermolysis, and MEA is regenerated [23]. Although MEA is the most popular technology for this purpose, it has multiple disadvantages, including high energy requirement for solvent regeneration, degradation of amines over passing time by SO_x, and the corrosive effect of amines upon equipment [18,24].

In physical absorption, a chemically inert solvent removes CO_2 without chemically reacting. Diethyl ethers of polyethylene glycol, methanol, and N-methyl-2-pyrolidone are three absorbents that have been used for physical absorption of CO_2 in Selexol, Rectisol, and Purisol processes, respectively [21]. According to Henry's Law, the amount a gas dissolved in a liquid is proportional to its partial pressure above the liquid, which means that as overpressure increases, so does the solubility of the gas. This governing law of physical chemistry describes why physical absorption is such an effective method for separating H_2 and CO_2 in pre-combustion capture techniques. Compared to chemical absorbents, the recovery of physical absorbents consumes less energy;

however, the performance of physical absorption is also lower [25].

4.2. Adsorption

Adsorption is a promising method for CO_2 capture from a gas stream using solid, rigid adsorbents that can tolerate the high temperatures of flue gas. Adsorption has gained notable attention due to low operational cost, lower energy demand, ease of handling, and general reliability. Physisorption (weak physical interactions) and chemisorption (stronger chemical bonding) are the dominant mechanisms of CO_2 adsorption from a gaseous component by solid adsorbents. Numerous materials, including carbon-based [26], metal organic frameworks [27], silica [27], polymer-based [28], immobilized amine [29], and zeolites [30] have been tested as prospective CO_2 adsorbents. High porosity and specific surface area, high selectivity towards CO_2, high regeneration capacity, and potential reusability are the main criteria for selecting a new adsorbent [31]. Although adsorption is a promising alternative to amine scrubbing, its applicability remains limited. One of the main obstacles is low adsorption capacity and selectivity of adsorbents in post-combustion processes with low CO_2 pressure. Saturation of active sites on the surface of adsorbents by moisture is another difficulty in CO_2 adsorption. Functionalization techniques have been applied to solve these issues by engineered adsorbents [32].

4.3. Membrane separation

Compared to conventional solvent absorption and adsorption methods, membrane technology is a newer approach, which has been explored for CO_2 separation in recent years. Membranes are very thin layers of organic (e.g. cellulose acetate and polymers) or porous inorganic materials (e.g. silica, carbon, and ceramic-based materials) with pore sizes ranging from 0.1 to 2 μm. Selectivity and permeability are the two primary characteristics to consider when designing membranes well-suited for CO_2 separation [33]. Polymeric membranes are highly selective, and have been more successful for CO_2 capture. Polybenzimidazole (PBI) is a polymeric membrane with high mechanical strength, and high thermal and chemical stability. PBI is currently used at the pilot scale for CO_2 separation based on the dissolution-diffusion principle [14]. Although membrane technology can be used to
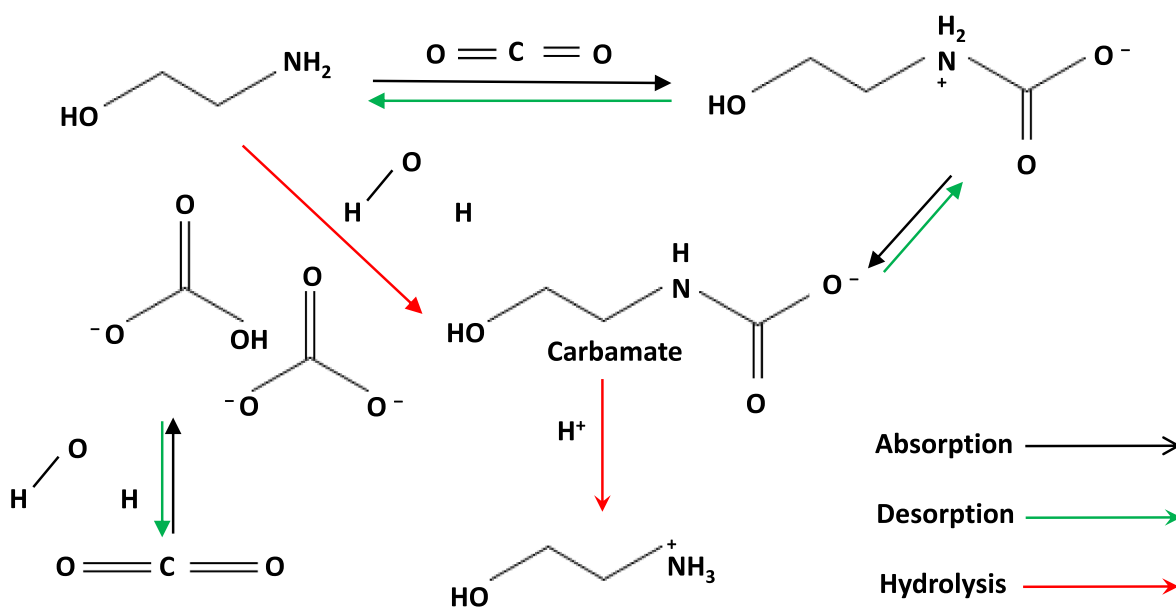

Fig. 2. Mechanisms of chemical absorption and desorption of CO_2 in MEA solution (Adapted from Lv et al. [23]).

separate CO_2 from syngas (CO_2/H_2), flue gas (CO_2/N_2), or natural gas (CO_2/CH_4), the CO_2 capture strategies significantly affect the operational cost. Overall, this technology is more appropriate for pre-combustion carbon capture with high gas pressure. It accrues greater expense when used in post-combustion processes due to the necessity of extra equipment to pressurize feed streams [24].

In addition to absorption, adsorption, and membrane methods, other techniques such as cryogenic distillation [34], chemical looping combustion [35], and hydrate-based gas separation [36] have been investigated for CO_2 capture. Likewise, each of these methods have their own advantages and disadvantages. For instance, cryogenic techniques are able to recover CO_2 with high purity without using reactive chemical solvents [37]. Although cryogenic methods are considered green technology, they are prohibitively expensive; the energy required to liquefy CO_2 at temperatures below $-70\,^{\circ}C$ often far outweighs the net gain from this method [38]. Pros and cons aside, these methods cannot yet compete with conventional methods on the industrial scale. Absorption by amine-based alkali solvents remains the dominant CO_2 capture method due to easy scale up and low cost. Regardless of which carbon capture method is used, the collected CO_2 must be purified, compressed, and transported for subsequent treatments. These processes are divided into carbon capture and storage (CCS); carbon capture, utilization, and storage (CCUS); and carbon capture and utilization (CCU); depending on whether the CO_2 is stored or upgraded.

5. Processing pathways of post-capture CO_2

5.1. Carbon capture and storage (CCS) and carbon capture, utilization, and storage (CCUS)

The history of CCS processes dates back to the 1970′s, when Nordhaus (1975) and later, his colleague Marchetti (1977), developed the idea of collecting, pipeline transporting, and storing CO_2 into deep ocean reservoirs or cavities of natural gas and oil [39]. Nordhaus' idea was awarded the 2018 Nobel Prize in economics for postulating the first economic model of global warming, which simultaneously highlights the profound importance of carbon capture as a concept [40]. The overarching aim of CCS is long-term storage of captured CO_2 from main point sources to prevent its emission to the atmosphere. Storage in the deep ocean storage and underground geological formations were determined to be the best locations for deep injection of CO_2, according to an IPCC Special Report on CCS published in 2005 [41]. A modern criticism of deep ocean storage is the risk of ocean acidification by CO_2 leakage. Geological storage capacity is estimated to be 675–900 Gt CO_2 for the depleted oil/gas fields and 1000–10,000 Gt CO_2 for deep saline formations [41]. Although CCS has already been verified as technically feasible, existing CCS technologies cannot efficiently reduce atmospheric CO_2 concentrations. A recent report counted just 19 active, large-scale CCS facilities with an annual storage capacity of 40 million tons, globally [42]. This equates approximately 0.1% of total annual CO_2 emission. The myriad difficulties of commercially deploying CCS technologies are correlated with the high operational costs of this technology [42]. Additionally, CO_2 escape from underground geological storage is yet another serious concern related to CCS methods. In this regard, newer technologies oriented towards CCUS (built upon CCS foundations) aim to reduce the expenses of carbon capture by utilizing concentrated CO_2. Enhanced oil recovery (EOR), enhanced gas recovery (EGR), enhanced coalbed recovery (ECBR), and enhanced water recovery (EWR) are four major CCUS applications at work in the energy industry today. During the process of oil extraction, even after hydraulic water injection, more than 50% of the total oil well remains belowground. CO_2 can be used instead of traditionally applied surfactants, nitrogen gas, or steam to recover the remaining oil, the economic turnover of which can be used to reduce the cost of CCS projects. Despite the economic utility, continued extraction of fossil fuels by EOR and EGR flagrantly contradicts of the spirit of sustainable CO_2 reduction. Both

CCS and CCUS are short-term partial solutions to reduce atmospheric CO_2 concentrations. Innovative, foundational approaches are needed to overcome the universal challenges of CO_2 emission.
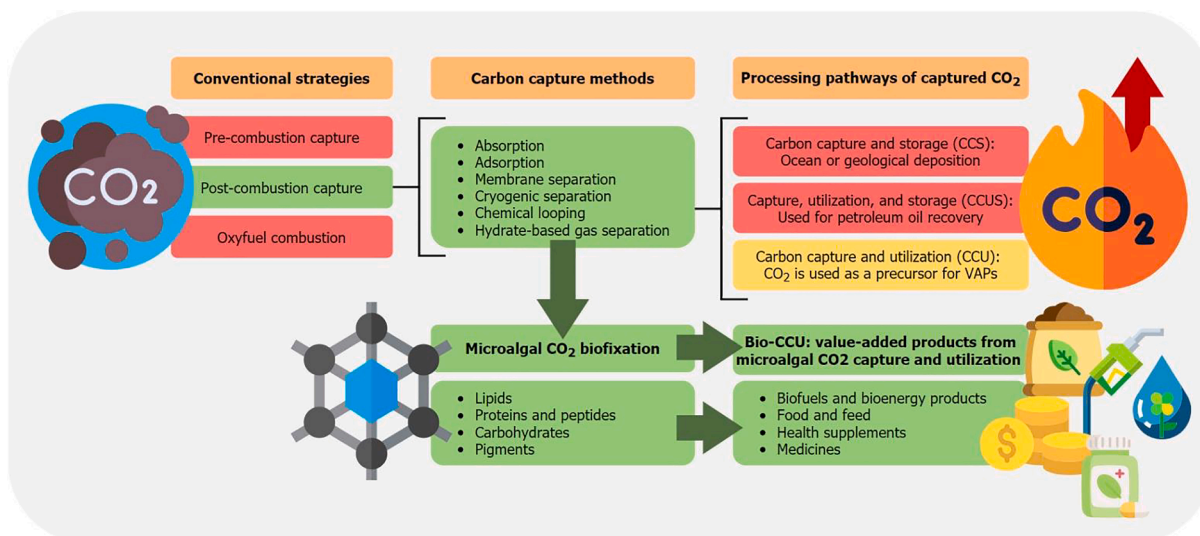
5.2. Carbon capture and utilization (CCU)

Contrary to CCS and CCUS approaches, CO_2 captured from emission point sources is upgraded to value-added products (VAPs) in the CCU process chain. Akin to CCS and CCUS, CCU reduces CO_2 emission, but, importantly, CCU decreases the consumption of exhaustible fossil resources and increases emissions-free economic value. CO_2 is a valuable precursor of VAPs such as gasoline, diesel, urea, methane, acetic acid, methanol, dimethyl ether, formic acid, dimethyl carbonate, and succinic acid through various processing pathways [43]. Available manufacturing pathways from CO_2 to VAPs include chemical, electrochemical, and photochemical reactions, as well as biological processes. Detailed reactions and pathways for abiotically converting CO_2 to VAPs via different technologies can be found in several previously published reviews [44–48]. Urea production, Sabatier synthesis (CO_2 methanation), hydrogenation to methanol, hydrogenation to formic acid, and dry reformation (syngas production) are several CO_2 conversion reactions, all of which are well-established for producing commonly used chemicals from CO_2 [48]. Organic carboxylation and reduction of CO_2 are endergonic reactions with a high kinetic barrier, meaning they require high amount of energy [49]. Despite the many advantages of CO_2 utilization, CCU remains a nascent technology with many obstacles to be overcome.

From the perspective of biology, however, photosynthetic organisms play a principal role in CO_2 sequestration, especially photosynthetic microorganisms such as microalgae. Prokaryotic photosynthesis evolved billions of years ago (eventually giving rise to eukaryotic photosynthesis) and naturally reformed the earth's entire atmosphere by consuming CO_2 and enriching it with oxygen. This highly diverse group of microorganisms has been employed to convert inorganic carbon (C_i) to organic carbon-based compounds via photosynthesis. Eukaryotic green algae, diatoms, and euglenoids, as well as prokaryotic cyanobacteria (henceforth, collectively described by the umbrella term 'microalgae') incorporate CO_2 to synthesize various biochemical compounds, including lipids, proteins, carbohydrates, pigments, and phenols. The carbon in the CO_2 molecule is thereby fixed to the molecular skeleton of these substances, where it performs different biological functions. Microalgal biomass enriched with numerous biochemicals can be upgraded to a diverse range of products, including food, feed, biofuels, biopolymers, cosmetic, biomedicine, and nutraceuticals [50]. Hence, microalgal carbon capture is a transformative strategy for creating opportunities from challenge, ultimately reducing CO_2 emission sustainably by converting it to saleable VAPs. Fig. 3 illustrates the direct and indirect incorporation of microalgae into CCU schemes. In Scenario 1, after combustion of carbon-based materials, flue gas is directly transferred to microalgae cultivation facilities. In Scenario 2, using physical and chemical methods, captured CO_2 can be utilized as a source of Ci for microalgae cultivation instead of being stored.

6. Photosynthesis: nature-made CCU technology

The evolution of chloroplasts enabled microalgae to develop into CO_2-consuming bio-factories which generate a wide array of organic compounds. Light-dependent and light-independent reactions work in synchroneity to accomplish photosynthetic CO_2 assimilation in microalgae [51]. These reactions take place in microalgal chloroplasts, organelles with a bi-layer membrane containing thylakoids and stroma. Thylakoids are disc-shaped sacs, which are surrounded by the liquid matrix of the stroma. Light-dependent reactions occur in thylakoids membranes to provide the required energy for CO_2 biofixation of during light-independent reactions [52]. Fig. 4 shows the bio-machinery of photosynthesis, including light-harvesting antennae, photosystem II

Fig. 3. Schematic overview of conventional carbon capture methods, and proposed route towards sustainable microalgal biological carbon capture and utilization. Abbreviations: CO_2, carbon dioxide; CCS, carbon capture and storage; CCUS, carbon capture, utilization, and storage; CCU, carbon capture and utilization; VAPs, value-added products; Bio-CCU, biological carbon capture and utilization. Color coding: red, unsustainable technology; yellow, possibly sustainable technology; green, the most sustainable technology.
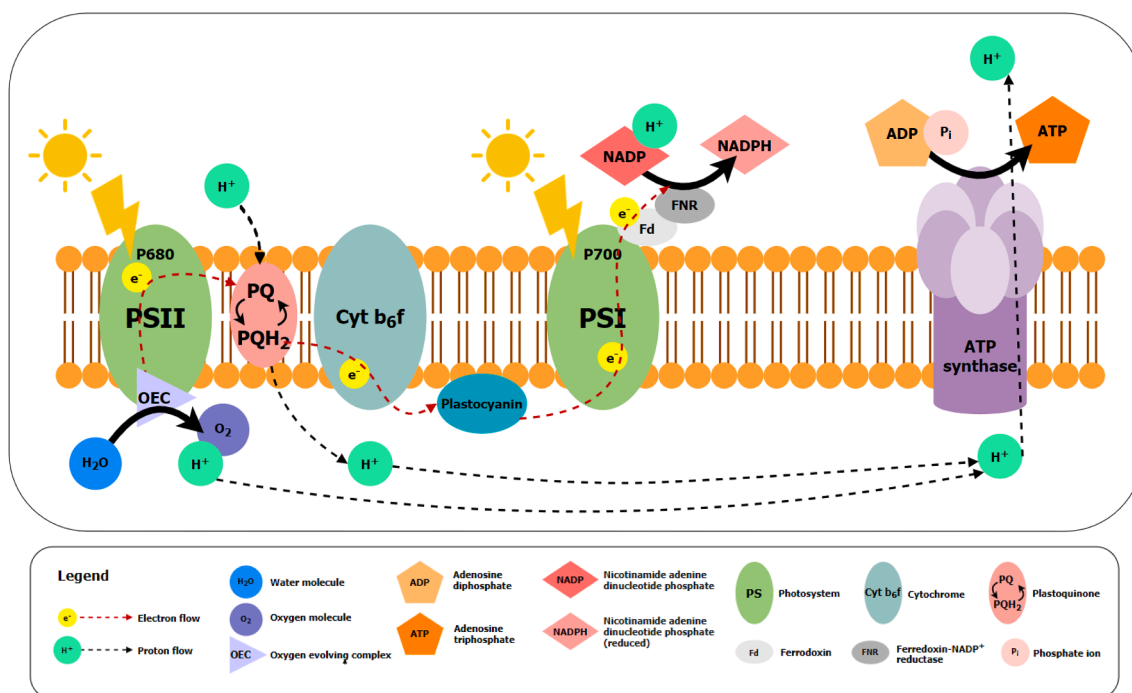

Fig. 4. Fundamental molecular pathways of oxygenic photosynthesis [57,145].

(PSII), cytochrome b6/f (cyt b6/f), photosystem I (PSI), and ATP synthase (ATPase), which are embedded in the thylakoid membrane [53]. PSII and PSI are protein-pigment super-complexes that absorb the energy of light and begin the electron transport chain (ETC) to reduce $NADP^+$ to $NADPH_2$ [52,54]. Photosynthesis is initiated when light-harvesting antennae absorb photons (light energy) and transfers them to the reaction center of PSII [55]. The reaction center contains a chlorophyll dimer with a photon absorption maximum wavelength of 680 nm (P680). As the primary electron donor, P680 is photo-oxidized (P680 + photon → $P680^+$ + e^-) and releases a pair of electrons [56]. Due to charge separation, the energized electrons are transferred to a pheophytin molecule, which in turn reduces plastoquinone (PQ-A); the

primary electron acceptor. The ETC continues as electrons move to PQ-B, the secondary electron acceptor [57]. PQ is reduced to plastoquinonol (PQH_2) by receiving two protons (H^+) from the stroma [58]. During the slowest reaction of the photosynthetic electron flow, PQH_2 is oxidized by cyt b6/f [57]. From Cyt b6/f complex, plastocyanin (PC) transfers an electron to PSI [57]. Delivering electrons to the reaction center of PSI (P700) results in an energy loss, creating a gradient for pumping H^+ from the stroma into the lumen (the liquid inside the thylakoid sac) [54]. In P700, the electron is excited again by receiving photons, and is transferred through a series of carriers (A0, A1, Fx, and FA/FB), ultimately arriving at ferredoxin (Fd). Ferredoxin-NADP$^+$ reductase (FNR) catalyzes the reduction of $NADPH_2$, the ultimate metabolite of the ETC,

which is then used as the biochemical reductant in light-independent reactions [57].

In a different reaction, a water molecule is split within the lumen by the oxygen-evolving complex (OEC). Water hydrolysis facilitated by the OEC releases electrons (e⁻), protons (H⁺), and diatomic oxygen (O₂, as a by-product) [59]. Electrons are used to recover the oxidized P680⁺. The H⁺ ions that accumulate in the lumen during the light-dependent reaction have a high energy potential, and flow back to the stroma through the action of ATPase [57]. ATPase is an enzyme that uses this energy to phosphorylate ADP to ATP, which is the primary source of chemical energy in light-independent reactions. Synthesis of $NADPH_2$ and ATP through the light-dependent reactions is represented by Eq. (1) [54]:

$$2NADP + 2H_2O + 3ADP + 3Pi \rightarrow 2NADPH_2 + 3ATP + O_2 \quad (1)$$
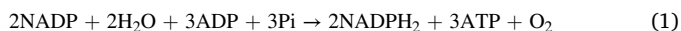
$NADPH_2$ and ATP are used during the light-independent reactions of the Calvin cycle. This biochemical process consists of three steps, which occur in the stroma of the chloroplast; carboxylation, reduction, and regeneration [60]. During carboxylation, CO_2 is added to ribulose 1,5-biphosphate (RuBP), a five-carbon compound with the chemical formula $C_5H_{12}O_{11}P_2$. The six-carbon compound which is synthesized by the addition of CO_2 to RuBP is chemically unstable, and decomposes into two molecules of 3-phosphoglyceric acid (3-PGA). The enzymatic reaction of carboxylation is catalyzed by RuBP carboxylase/oxygenase (RuBisCO) [61]. During the subsequent reduction phase, 3-PGA is converted into a three-carbon sugar molecule, glyceraldehyde-3-phosphate (GA3P) in a two-step process. First, ATP is used for the phosphorylation of 3-PGA into 1,3-bisphosphoglyceric acid (1,3BPG) or glyceraldehyde-P. The intermediate compound 1,3BPG is then reduced to GA3P by the reducing power of $NADPH_2$ [62]. During regeneration, most of the GA3P is transformed into RuBP through a series of complex enzymatic reactions with intermediates of 3-, 4-, 5-, 6-, and 7-carbon sugar phosphates [63]. The remaining GA3P is stored in the form of starch within the chloroplast. Carbohydrates are the primary end-product of photosynthesis, but CO_2 is also incorporated into other compounds, including fatty acids, organic acids, and amino acids. Non-carbohydrate end-products of photosynthetic CO_2 fixation are highly dependent upon cultivation conditions, such as nutrient profiles of wastewater, light intensity, and CO_2/O_2 concentrations [54].

7. Applying carbon capture biology: Bio-CCU

While the previous section detailed how photosynthesis sequesters CO_2 directly (biological CCU), simple diffusive uptake of dissolved CO_2 in microalgae is relatively rare in nature, although microalgal cells have a high affinity for CO_2 molecules. Most microalgal species grow best at a pH range between 7.0 and 8.4 [64,65], conditions under which the majority of inorganic carbon is available as bicarbonate ions (HCO_3^-)

Table 1
CO_2 bio-fixation efficiency by various microalgae species under different experimental conditions.

Species	CO_2 %	Aeration rate	CO_2 biofixation rate	Temperature (°C)	Initial pH	Culture medium	Biomass production	References
Botryococcus braunii	10% mixed with N_2	0.1 vvm	356 mg/L/day	20	–	BG11	0.41 g/L	[117]
	20% mixed with N_2	0.1 vvm	532 mg/L/day	20	–	BG11	0.26 g/L	
Scenedesmus sp.	10% mixed with N_2	0.1 vvm	347 mg/L/day	20	–	BG11	0.90 g/L	
	20% mixed with N_2	0.1 vvm	2177 mg/L/day	20	–	BG11	1.95 g/L	
Heynigia riparia SX01	0.03% (Ambient air)	0.13 vvm	0.27 g/L/day	28	8	BG-11	1.28 g/L	[118]
	5% mixed with air	0.13 vvm	0.37 g/L/day	28	8	BG-11	2.37 g/L	
	10% mixed with air	0.13 vvm	0.46 g/L/day	28	8	BG-11	2.76 g/L	
	15% mixed with air	0.13 vvm	0.71 g/L/day	28	8	BG-11	3.28 g/L	
Chlorella vulgaris ESP-31 (wild type)	Simulated flue gas containing 25% CO_2	0.1 vvm	53.35 mg/L/day	40	7.4	BG-11	0.15 g/L	[119]
Chlorella vulgaris ESP-31 (mutant 283)	Simulated flue gas containing 25% CO_2	0.1 vvm	272.06 mg/L/day	40	7.4	BG-11	0.78 g/L	
Chlorella vulgaris ESP-31 (mutant 359)	Simulated flue gas containing 25% CO_2	0.1 vvm	194.03 mg/L/day	40	7.4	BG-11	0.64 g/L	
Dunaliella salina	Ambient air	0.5 vvm	0.055 g/L/day	24	8	f/2 medium	~ 0.22 g/L	[68]
	6% mixed with air	0.5 vvm	0.067 g/L/day	24	8	f/2 medium	~ 0.26 g/L	
	20% mixed with air	0.5 vvm	0.016 g/L/day	24	8	f/2 medium	~ 0.09 g/L	
	20% mixed with N_2 (constant flow rate)	0.5 vvm	0.043 g/L/day	24	8	f/2 medium	~ 0.30 g/L	
	20% mixed with N_2 (gradual increasing CO_2 level)	0.5 vvm	0.106 g/L/day	24	8	f/2 medium	~ 0.16 g/L	
Chlorella vulgaris P12	2% mixed with air	0.4 vvm	1.5 g/L/day	30	7	Synthetic medium	6.90 g/L	[120]
	6% mixed with air	0.4 vvm	2.29 g/L/day	30	7		10 g/L	
	10% mixed with air	0.4 vvm	1.93 g/L/day	30	7		8.60 g/L	
Chlorella sp.	Flue gas containing 10% CO_2	0.5 vvm	261 mg/L/day	28	8.1	Domestic wastewater + poultry waste	1.20 g/L	[121]
Scenedesmus obtusiusculus	Flue gas containing 4–5% CO_2	–	111.4 mg/L/day	28	8	BG-11	1.09 g/L	[122]
Chlorella vulgaris (ISC-23)	6% mixed with air	0.5 vvm	3.222 g/L/day	27	7.4	BG11	14.30 g/L	[123]
Chlorella sp. LAMB 31 (high-CO2 tolerant strain)	40% mixed with air	–	0.144 g/L/day	26	6	BG11	~ 1 g/L	[124]
Chlorella sp. LAMB 122 (high-CO2 non-tolerant strain)	40% mixed with air	–	0.017 g/L/day	26	6	BG11	~ 0.32 g/L	
Chlorella sp. C-1 (control set)	Ambient air	0.5 vvm	0.357 g/L/day	30	7–8	3N-BBM	1.22 g/L	[125]
Chlorella sp. E–1 (experimental set)	Flue gas containing 10% CO_2	0.5 vvm	0.469 g/L/day	30	7–8	3N-BBM	1.69 g/L	

[66]. Dissolved CO_2 may comprise less than 1% of total dissolved inorganic carbon when the medium is in equilibrium with the atmosphere. Due to this natural diffusivity, microalgae have developed several carbon-concentrating mechanisms (CCMs), which are generally advantageous for biologically-mediated carbon capture. Carbon acquisition in microalgae occurs via three main pathways; active, direct uptake of HCO_3^-, an active CO_2 transport mechanism, and a carbonic anhydrase (CA) enzyme external to the plasma membrane [66].

Several key factors influence microalgal photosynthetic efficiency and CO_2 assimilation, including heat, light, and mass transfer of CO_2 and nutrients. In this respect, physico-chemical (e.g. pH, temperature, salinity, turbidity) and nutrient profiles of culture media, properties of flue gas (e.g. CO_2 concentration, temperature, toxic compounds), light wavelengths and penetration, bioreactor design, and selection of microalgae species significantly influence microalgal CO_2 biofixation. Several important factors which influence microalgal growth and rate of CO_2 biofixation are presented in Table 1.

The availability of macro- and micronutrients nutrients in microalgal cultivation media, both deficiency and excess, also strongly affects biological maintenance, growth, and photosynthetic efficiency. This is due to the vital role of certain elements in different metabolic pathways. For instance, nitrogen (N) is necessary for the synthesis of ATP, protein, nucleic acid, and various enzymes. Phosphorus (P), another macronutrient, is utilized by microalgae for the phosphorylation of ADP and as backbone of many biomolecules such as NADPH, RNA, DNA, phosphoproteins, phospholipids, and polyphosphates. Deficiency or depletion of either N or P can therefore be detrimental to photosynthetic rate and carbon cycling. Likewise, some micronutrients and trace elements such as copper (Cu), zinc (Zn), nickel (Ni), manganese (Mn), cobalt (Co) are necessary for diverse metabolic functions which affect photosynthesis and subsequent microalgal growth [67]. Nutrient-enriched wastewaters and flue gas can provide most essential nutrients (macro and micro) and inorganic carbon (C_i, an indispensable substrate of photosynthesis) for microalgal growth. Flue gas can provide a rich source of C_i; however, elevated CO_2 levels, excessive NO_x/SO_x content, and high temperatures of flue gas are three characteristics that can negatively affect photosynthesis. Generally, CO_2 concentration ranges between 10 and 25% in flue gas, which is higher than the average optimum concentration (2–6%) for microalgal growth [68]. Injecting high-CO_2 flue gas directly into microalgal ponds and bioreactors can decrease the pH of the culture medium. Such elevated CO_2 levels (>10%) and the resultant acidification damages RuBisCO in microalgal CCMs, the key enzymatic driver of photosynthesis, and therefore causes growth inhibition and cell death [69,70].

Temperature is another important parameter which strongly affects microalgal photosynthesis; most microalgal species grow best at a temperature optimum between 15 and 30 °C , and cannot perform effectively at temperatures $\geq$ 35 °C [71]. Rates of growth and CO_2 biofixation of wild type microalgae at high temperatures (40 °C) are significantly lower than thermo-tolerant mutants, such as C. *vulgaris* ESP-31. Direct injection of high-temperature flue gas increases the temperature of culture media well beyond that range, detrimentally affecting multiple aspects of microalgal growth and metabolism; such as nutrient absorption and utilization efficiency, enzyme activity, and, ultimately, CO_2 biofixation. In a recent study, the CO_2 fixation rate of *Spirulina* sp. increased from 25.5 to 51.3 $g/m^2/d$ when the cultivation temperature was raised from 23.8 to 33 °C, but subsequently decreased to 39.0 $g/m^2/d$ by a further increase to 38 °C [72]. Additionally, CO_2 solubility is reduced at temperatures above 20 °C. When emitted to the atmosphere, flue gas temperatures can be as high as 60–110 °C; temperatures that necessitate significant cooling of the flue gas prior to injection into microalgae ponds or photobioreactors [73].

Another challenge associated with utilizing flue gas for microalgae cultivation is the inhibitory effect of sulfur oxides (SO_x) and nitrogen oxides (NO_x) on microalgae growth. A study conducted by Camargo and Lombardi [74] demonstrated the sensitivity of microalgae to these compounds, by comparing flue gas at concentrations of 0 (control group) to 0.1, 0.3, and 0.8 L/d. They found no significant difference in growth and productivity in the 0.1 and 0.3 L/d treatments with respect to the control, but increasing the injection concentrations to 0.8 L/d reduced microalgal productivity by 62% compared with the lower concentration groups. The negative effects of high concentrations of these compounds may be related to medium acidification or toxic effects on microalgal cells. Sulfur dioxide (SO_2), the most abundant SO_x compound in flue gas, can lower the pH of culture media by forming bisulfite (HSO_3^-) in a low-buffered medium such as wastewater [75]. Conventionally, phosphate buffers have been used to control SO_2-affected pH in microalgal growth media [76], and toxic NO (the most abundant NO_x compound) has been chemically oxidized to more bioavailable NO_3^- [77], in order to control the most detrimental effects of NO_x and SO_x. Blending flue gas with other gases containing low concentrations of O_2 is another strategy for reducing the toxicity of NO_x and SO_x, as well as neutralizing some adverse effects of high CO_2 concentrations [68,78]. Effective, efficient, biologically-mediated post-combustion carbon capture is near impossible to achieve without an intermediary storage step due to high temperatures, pH levels, and concentrations of inorganic carbon species.

Even when flue gas is bubbled directly into liquid media, CO_2 has a low solubility in water, and much of it is still lost to the atmosphere. Amine scrubbing (chemical capture technique, as discussed in *Section 4.2.* (Absorption), can conveniently provide two essential nutrients for microalgal growth; bioavailable nitrogen and inorganic carbon, in the form of ammonium carbonate. Microalgae preferentially use ammonia or ammonium over other nitrogen sources, such as nitrate or nitrite, and most microalgal CCMs are extremely efficient in bicarbonate uptake. Additionally, using amine scrubber condensate for microalgal cultivation circumvents the need for expensive (and ultimately wasteful) amine solvent regeneration. The primary obstacle in this approach is the high pH of condensate, which, even when used to cultivate halo-tolerant microalgae, results in severely restricted growth rates. Fortunately, this challenge can be overcome with the simple dilution of condensate with an acidic wastewater. A recent study [79] used acidic soybean wastewater as both a nutrient source and pH regulator to dilute condensate collected from an amine scrubber. This process resulted in an impressive 78.8 mg/L/d biomass yield, a carbon conversion efficiency >60%, and a reduction in ammonia escape from the amine scrubbing process, down to 15.8% [79].

Selecting appropriate microalgae species compatible with flue gas and wastewater conditions is another factor that can greatly improve the efficiency of CO_2 biofixation. Microalgae (described in *Section 5.2.* as an umbrella term for eukaryotic green algae, diatoms, and euglenoids, as well as prokaryotic cyanobacteria) display extraordinary biodiversity, exhibiting significant differences in genetics, cellular physiology, and metabolic potential across various species and strains [80]. As such, the tolerance of microalgae to the conditions caused by high concentrations of CO_2 and flue gas compounds (SO_x and NO_x) is often species-specific. Some species are adaptable; i.e. capable of developing mechanisms to protect their photosynthetic enzymes against acidic conditions caused by elevated levels of CO_2, NO_x, and SO_x. These mechanisms include active proton (H^+) pumping from cytoplasm to vacuoles, controlling the pH of their environment (the liquid medium) by excreting metabolites, and downregulating their CO_2-concentrating mechanisms [81]. It has been reported that *Desmodesmus armatus* can develop alkalization activity by accumulating metabolites such as d-glyceric acid, l-malic acid, fumaric acid, gluconic acid, oxamic acid, and lipoic acid under elevated CO_2 concentrations [82]. Moreover, some microalgae species have been observed to build a tolerance to higher CO_2 concentrations through gradually increasing CO_2 concentrations with respect to cultivation times. For example, the CO_2 tolerance of *Dunaliella salina* was artificially enhanced from 6% to 30% by slowly increasing injection concentrations over time [68]. The biofixation rate was significantly higher when CO_2 concentrations were gradually increased (up to a maximum 0.106 g/L/

d) as compared to a constant flow rate (0.043 g/L/d).

To this point, it is noteworthy to add that exposure of a microalgal species to flue gas conditions could activate several genes through adaptive evolution, which thereby enhance the species' tolerance to high CO_2, NO_x, and SO_x concentrations. An experimental example was recently demonstrated by cultivating *Chlorella* sp. Cv under simulated flue gas for 46 generations. Later generations exhibited upregulation of genes related to nitrogen and sulfur metabolism enabling them to utilize nitrate and sulfate from NO_x and SO_x [83]. Microalgae (and microalgal consortia) have long been known to adapt well to changing conditions, following well-established principles of community ecology even within artificial ecosystems, e.g. bioreactors [84]. Indeed, capitalizing upon these natural dynamic abilities to adapt and compete has been suggested as the best way forward in realizing successful microalgal productivity on the pilot scale [85], and should be further explored as a biological tool for maximizing carbon sequestration potential.

8. Valorizing microalgal biomass

8.1. Microalgal value-added products

Within the term 'carbon capture and utilization', the word utilization refers to actively using microalgal biomass as a precursor for a multitude of microalgal-based bioproducts. Microalgal cells incorporate captured carbon into a variety of macromolecules, metabolites, and other biochemical compounds; including lipids, proteins, polysaccharides, pigments, cellulose, RNA (ribonucleic acid), and DNA (deoxyribonucleic acid) [86]. Consequently, microalgal biomass is enriched with high-value compounds, which can be upgraded to a diversity of value-added products (VAPs). Therefore, bio-CCU is not simply a CO_2 mitigation strategy, it is a synchronized approach to climate recovery and value creation by generating saleable microalgal VAPs [87].

To this end, a concept which has gained popularity in recent years is that of the "biorefinery". Defined under the IEA's Task 42 on Biorefining in a Circular Economy, *"biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy"* [88]. This approach targets zero-waste bioproduction by valorizing every side stream generated during the processing pathway towards a target product. Once harvested, the most efficient way to process raw microalgal biomass is by employing the biorefinery approach. Table 2 summarizes various biochemical compounds derived from microalgal lipids, proteins, polysaccharides, and pigments, as well as practical applications of each.

Microalgal lipids are frequently targeted as a valuable biomass fraction, and are generally produced in abundance, as they comprise elements of cell membranes, storage products, and various metabolites [89]. Dry microalgal biomass is composed of 3–20% lipids, and this approximate value can be enhanced to more than triple depending on microalgae species (in oleaginous algae) and cultivation conditions (light, CO_2 concentrations and nitrogen deficiency) [90]. The primary constituents of crude microalgal lipids are triacylglycerols, glycolipids, and phospholipids. These compounds are composed of glyceride and

Table 2
Value-added products from microalgal biomass and their applications.

Microalgae	Compounds	Formula	Class	Application	References
Chlorella sp. and *Scenedesmus* sp.	Palmitic acid	$C_{16}H_{32}O_2$	Lipids	Biodiesel production	[126]
Chlorella sp. and *Scenedesmus* sp.	Oleic acid	$C_{18}H_{34}O_2$	Lipids	Biodiesel production	
Pseudokirchneriella subcapitata	Linolenic acid	$C_{18}H_{30}O_2$	Lipids	Health beneficial	[127]
Nannochloropsis oculate, Pavlova salina, Skeletonema costatum	Eicosapentaenoic acid	$C_{20}H_{30}O_2$	Lipids	Human diet supplementation	[128]
Schizochytrium sp., *Cryptecodinium cohnii, Pavlova salina*	Docosahexaenoic acid	$C_{22}H_{32}O_2$	Lipids	Medical and healthcare value	[128,129]
Porphyridium purpureum, Euglena gracilis, Parietochloris incisa	Arachidonic acid	$C_{20}H_{32}O_2$	Lipids	Beneficial health effects	[130]
Dunaliella Salina	β-carotene	$C_{40}H_{56}$	Pigments	Food pigments, precursor of vitamin A, potent antioxidants	[131]
Scenedesmus sp.	Lutein	$C_{40}H_{56}O_2$	Pigments	Food additives	[132]
Haematococcus pluvialis	Astaxanthin	$C_{40}H_{52}O_4$	Pigments	Coloring agent in aqua-feed, Cosmetic ingredient, Nutraceutics additive	[133]
Mallomonas sp.	Fucoxanthin	$C_{42}H_{58}O_6$	Pigments	Beneficial health effects	[134]
Spirulina platensis	Phycocyanin	–	Pigments	Nutrients and healthcare value	[135]
Porphyridium cruentum	Sugars (e.g. glucose, galactose, mannose, xylose)	$C_6H_{12}O_6$ $C_5H_{10}O_5$	Carbohydrates	Bioethanol production	[136]
Chlamydomonas reinhardtii	Starch	$(C_6\text{-}H_{10}\text{-}O_5)_n$	Carbohydrates	Bioethanol production Starch-based bioplastic production	[137,138]
Nannochloropsis oceanica	Cellulose	$(C_6\text{-}H_{10}\text{-}O_5)_n$	Carbohydrates	Cellulose nanofibrils	[139]
Isochrysis galbana	Laminarin (β-glucan)	$C_{18}H_{32}O_{16}$	Carbohydrates	Biomedical	[140]
Tisochrysis lutea, Nannochloropsis gaditana, Tetraselmis suecica, Scenedesmus almeriensis, Tetraselmis chuii	Essential amino acids (threonine, methionine, valine, leucine, lysine)	$C_4H_9NO_3$ $C_5H_{11}NO_2S$ $C_5H_{11}NO_2$ $C_6H_{13}NO_2$ $C_6H_{14}N_2O_2$	Protein	Food, feed, and aqua-feed ingredients	[97,141]
Tisochrysis lutea, Nannochloropsis gaditana, Tetraselmis suecica, Scenedesmus almeriensis, Tetraselmis chuii	Non-essential amino acids (cysteine, aspartic acid, proline, glutamic acid, arginine)	$C_3H_7NO_2S$ $C_4H_7NO_4$ $C_5H_9NO_2$ $C_5H_9NO_4$ $C_6H_{14}N_4O_2$	Protein	Food, feed, and aqua-feed ingredients	[97,141]
Pavlova lutheri, Arthrospira platensis, Tetradesmus obliquus, Tetradesmus obliquus	Peptide sequence (MGRY, PNN, WPRGYFL, SDWDRF)	–	Protein	Bioactive agents, antioxidant	[142]
Nodularia spumigens, Pseudonitzchia spp., *Aphanizomenon flos-aquae*	Anatoxin-a(s), Domoic acid, Nodularin	$C_7H_{17}N_4O_4P$ $C_{15}H_{21}NO_6$ $C_{41}H_{60}N_8O_{10}$	Protein	Toxins	[143]

valuable fatty acid (FA) molecules. Microalgal FAs may be saturated (without double carbon bonds in the carbon chain), monounsaturated (one double bond) and polyunsaturated (more than one double bond); for example, carboxylic acid chains contain 12–22 carbon atoms [91]. FAs can be used as the base materials of many products with diverse applications, from nutraceuticals to biofuels. Biodiesel derived from microalgal lipids has received universal attention as a promising alternative to fossil-based fuels, especially because of its potential for fuel blending, which allows for gradual phasing into the transport fuel market. During biodiesel production, microalgal lipids are converted to fatty acid methyl esters (FAMEs) via the chemical reaction of transesterification. Two important FA characteristics which directly affect biodiesel properties are degree of saturation (number of carbon double bonds) and total number of carbon atoms in the lipid chain [92]. FAs with carbon chain length ≤19 are more appropriate for biodiesel production, while FAs with carbon chain length ≥20 are more suitable for nutritional supplements (e.g. vegan omega fatty acid products). Microalgae produce beneficial polyunsaturated fatty acids (PUFAs) such as ω-3 (eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA)) and ω-6 (arachidonic acid) with 20 and 22 carbon atoms, respectively, and each are fundamental in human nutrition [93].

Amino acids, peptides, and proteins are other valuable constituents of microalgal biomass; these are valuable as food and feed supplements. The species *Spirulina maxima*, *Spirulina platensis*, *Chlorella vulgaris*, and *Scenedesmus obliquus*, with high protein contents of 60–71%, 46–63%, 51–58%, 50–56%, respectively, have been used to produce humangrade protein and phytonutrient supplements on an industrial scale for decades [94,95]. Farther back in human history, *Spirulina* sp. have been recognized as a nutrient-dense food supplement (traditionally incorporated into bread) more than 700 and 1000 years ago in Mexico and Asia, respectively [90]. In our modern era, microalgal protein has been marketed as a beneficial human health product since the 1950′s. Microalgal proteins have long been known to contain essential amino acids (EAAs) such as threonine, methionine, isoleucine, valine, leucine, lysine, and histidine, none of which are synthesized by human bodies. Especially for those eating vegan diets, which are commonly proteindeficient, microalgal protein can provide an ideal plant-based source of diverse amino acids. In addition to EAAs, microalgal protein also contains non-essential amino acids (NEAAs), such as arginine, proline, glutamic acid, aspartic, cysteine, and glycine, which have additional health benefits [96], especially for athletes. The ratios of EAAs/NEAAs in the amino acid profile of *Tisochrysis lutea*, *Nannochloropsis gaditana*, *Tetraselmis suecica*, and *Scenedesmus almeriensis* have been reported 0.88, 0.87, 0.88, and 0.87, respectively [97].

Protein-derived bioactive compounds, such as peptides, are also possible to extract from microalgal biomass. These are short chain proteinogenic amino acids with multiple applications in pharmaceutical, cosmetic, and food industries. Recently, Montalvo et al. [98] reported antioxidant (prevents free-radical damage), chelating, antimicrobial, anti-inflammatory, and anti-collagenase (prevents collagen breakdown) properties of three peptides extracted from *Arthrospira maxima* OF15 biomass [98].

Carbohydrates are another major biomass fraction derived from microalgae. Carbohydrates are carbon-rich biomolecules which can be used as precursors for a diversity of commercial products. Detailed in *Section 6*, CO_2 is incorporated into three-carbon compounds (GA3P) which are used as substrates to form monosaccharides, such as glucose. Monosaccharides are the building blocks of much larger polysaccharides, such as starches and cellulose. Microalgae use carbohydrates as energy reservoirs, and also incorporate them as structural components of cell walls. Glycogen (α-1,4 linked glucan), floridean starch (a hybrid molecule composed of starch and glycogen), and amylopectin-like polysaccharides (starch) are some storage carbohydrates found in cyanobacteria, red algae, and green algae, respectively [99]. Acid hydrolysis of the biomass from several species (*Phaeodactylum tricornutum*, *Nannochloropsis salina*, *Chlorella vulgaris*, *Scenedesmus*

ovalternus, *Porphyridium purpureum*, and *Dunaliella salina*) of green algae has yielded a diverse range of monosaccharides, including glucose, galactose, rhamnose, mannose, ribose, glucuronic acid, glucosamine, xylose, and fucose [100]. Starch and other fermentable sugars derived from microalgal biomass are a strong feedstock candidate for renewable bioethanol production by *Saccharomyces cerevisiae* (yeast) fermentation, one of the oldest biotechnologies in human history. Apart from their potential for bioethanol production, some carbohydrates of microalgae exhibit antiviral, antibiotic, antiparasitic, anti-inflammatory, and anticancer properties. Among these, sulfated polysaccharides extracted from *Porphyridium* sp. and *Nannochloropsis oculata* are known to contain D- and L-Gal, D-Glc, D-Xyl, D-GlcA, and sulfate groups, which show antiviral, antitumoral, and immunostimulatory properties [101]. Low production costs, safety, minimal cytotoxicity, a broad antimicrobial spectrum, and acceptability are notable advantages of sulfated polysaccharides. Another type of commercially-valuable compounds extracted from microalgal biomass are pigments, with three major classes; chlorophylls (*a*, *b*, *c*, and *d*), carotenoids (α-carotene and β-carotene), and phycobilins. In addition to these main classes, luteol, fucoxanthol, peridinin, phycoerythrins, and phycocyanins also have been extracted from some species of red microalgae, diatoms, and cyanobacteria [102]. Microalgal pigments have been used as antioxidant/ anti-inflammatory agents, immune activators, and vitamin precursors for decades. Often collectively called "phytonutrients", microalgal pigments are widely used as food and feed supplements, food coloring, and additives in pharmaceutical and cosmetic products [103]. While microalgae produce pigments (necessary for photosynthesis), some species (e.g. *Hematococcus* sp. and *Dunaliella* sp.) produce them in much higher quantities [104]. Although the concentration of pigments per unit dry biomass is lower than that of the aforementioned microalgal biomass fractions (lipids, proteins, and carbohydrates), pigments are much more commercially valuable [105]. The price of 1 kg of β-carotene and astaxanthin, each potent antioxidants, may be as high as €1370 and $2500, respectively [106].

Finally, microalgae (especially the subgroup of photosynthetic bacteria, cyanobacteria) produce small quantities of potentially valuable metabolites. Bioplastic precursors such as polyhydroxyalkanoates (PHAs), and, specifically, polyhydroxybutyrate (PHB), are highly valued for producing biodegradable plastic products. Although several genera of cyanobacteria (*Spirulina*, *Aphanothece*, *Gloeothece*, and *Synechococcus*) are confirmed to produce these precursor molecules, they constitute only a miniscule fraction of biomass produced, and are difficult to recover efficiently due to small sizes of both cyanobacterial cells and PHA/PHB granules.

Cyanobacterial genera such as *Synechocystis* and *Synechococcus* are also known to produce volatile organic compounds (VOCs), such as alkanes [107], alkenes [108], and decanes [109], which are highly valuable as energy-dense fuels and industrial solvents. Akin to cyanobacterial PHAs and PHB, however, these compounds are produced at extremely low concentrations. Previous studies focusing on PHB and VOC production have recommended future efforts in metabolic engineering to amplify genes that produce these compounds [108-110].

8.2. Carbon footprint vs. carbon handprint

A common term in carbon economics is "carbon footprint", which is generally used to describe the amount of CO_2 consumer goods or services emit to the atmosphere over the course of their respective life cycles. Companies that produce packaged products are becoming increasingly interested to include "carbon-friendly" badges on their labels; a status that must be certified by a third party, much like organic certification. Carbon-friendly products may simply be manufactured in a low-impact way, but, more often, companies invest in carbon offsetting (e.g. tree planting projects) to compensate for the emissions generated by manufacturing their products. This type of calculation is far from exact, and has set a worrisome precedent for buying one's way out of

climate-responsible industry practices. Moreover, "carbon footprint" is a term with a negative connotation to most consumers, creating a sense of guilt. A smarter business strategy to encourage climate-forward practices from the factories to customers is developing with the phrase "carbon handprint". Unlike the carbon footprint, the carbon handprint of a product quantifies how much carbon the product has already removed, either by using emissions-negative energy in manufacturing, or by being a product that is itself made from sequestered CO_2, such as the VAPs discussed above.

The carbon footprints and handprints of microalgal technologies are contentious. At face value, microalgae sequester carbon via photosynthesis, as discussed in detail throughout this review, suggesting a low (or nonexistent) carbon footprint and high carbon handprint. However, if not designed with some carbon-conscious foresight, even the process of microalgal cultivation can create carbon emissions. In colder, darker climates, microalgal cultivation requires sources of heat and light in order to grow effectively. If these conditions are met with energy-intensive artificial lighting and heat, especially if powered by non-renewable energy, the process may generate more emissions than it sequesters. However, Ekendahl et al. [111] demonstrated that year-round, outdoor cultivation of microalgae was possible as far north as Borås, Sweden, by providing heat and carbon from waste heat and flue gas, respectively, from a pulp and paper mill. They reported a maximum photosynthetic efficiency of 1.1%; due to this comparatively low productivity, the biomass was harvested just once per year. Despite relatively low photosynthetic efficiency, this study is important for establishing carbon-sequestering practices for microalgal cultivation, even at higher latitudes. They reported a mix of trophic strategies (i.e. autotrophic, mixotrophic, and heterotrophic) used in the indigenous microalgal consortia they employed, and recommended their approach for future carbon capture and energy storage [111]. Other studies have explored novel bioreactor configurations to maximize mass transfer of carbon from the media into microalgal biomass or metabolites. Deprá et al. [112] designed a hybrid photobioreactor, incorporating a bubble column and an "illumination platform", inspired by recent developments in biofilm cultivation strategies. In their model, a rough-surfaced platform is integrated into the circulation system, which greatly increases the surface area to volume ratio for the period of time that the microalgal cells flow over the platform. This configuration resulted in an average CO_2 conversion rate of 45.32 kg $CO_2/m^3/d$, and, interestingly, only 1.28% of the CO_2 was incorporated into biomass. A majority of converted CO_2, 82.75% of carbon mass transfer, was used to form volatile organic compounds (VOCs) [112]. The impressive VOC yield is somewhat unusual for *Scenedesmus obliquus*, the microalga used in this study; the genus *Scenedesmus* is often targeted for lipid accumulation rather than VOC production [113,114].

Similar to the carbon costs of cultivation, the carbon footprint of each subsequent microalgal processing stage (harvesting, dewatering, upgrading) must be balanced such that the final products are emissions-negative, i.e. have a net positive carbon handprint. Lifecycle analysis (LCA) is an important tool for carbon- and energy-balancing any bio-CCU system, thereby ensuring a positive carbon handprint. Developing sustainable, green practices is imperative for creating a carbon–neutral future, and, if sensibly designed and operated, microalgal biorefineries can positively contribute to these advances.

9. Research needs and future perspectives

Multiple obstacles must yet be overcome in order to establish the microalgal biorefinery as a universally applicable method for CCU on the industrial scale. Microalgae fix approximately 183 tons of CO_2 per 100 tons of dried microalgal biomass produced [115], but the first challenge to effectively exploiting this ability is making high concentrations of CO_2 bioavailable to microalgae at a stable rate. To this end, carbon capture methods require further study and refinement. Methods such as amine absorption and physical adsorption both hold potential

for transferring CO_2 into liquid microalgal growth media, but each have their respective drawbacks related to their CO_2 capture well before the CO_2 reaches microalgal bioreactors. Amines are known to be particularly corrosive, while adsorbents are less effective for CO_2 capture due to limited selectivity. Furthermore, there is little research available regarding the mass transfer efficacy from adsorbents to pH-neutral microalgal growth media; this knowledge gap must be filled before CO_2 adsorption can be used in tandem with microalgal bio-CCU. Other CO_2 capture techniques, such as membrane separation and cryogenic distillation, are simply too costly to be offset by the economic returns of microalgal VAPs. If future research can address the fiscal and energetic costs, however, these methods are technically compatible with microalgal bio-CCU.

To offset the monetary expenses of microalgal cultivation for bio-CCU, microalgal biomass can be upgraded to vast array of saleable bioproducts. Renewable energy is an attractive upgrading pathway; conventionally, microalgal lipids have been targeted for biofuel production [90]. Diligent research over the past two decades has consistently improved upon several shortcomings of microalgal bioproduction, with lipid-extracted residues used to create other forms of bioenergy, such as biogas via anaerobic digestion or alcohols via fermentative pathways. Still other research has investigated applying hydrothermal processing techniques (traditionally used to upgrade petroleum fuels) to whole microalgal biomass to create liquid biofuels with more favorable combustion properties, although this pathway is not yet commercially viable due to the energy requirements and fiscal cost of hydrothermal upgrading combined with low biofuel yield as compared with its petroleum counterparts [116].

Beyond bioenergy, microalgae are already highly valued for nutritional supplements like vegan omega fatty acid supplements, phytonutrients like chlorophyll and phycocyanin with anti-inflammatory and antioxidant properties, and high-quality protein. Microalgal polymers, such as PHAs and PHB have shown great promise for bioplastic production; however, low yields and difficulties with harvesting and purification are currently prohibiting efficient bioplastic production from microalgae beyond the laboratory scale [110].

This review has clearly established the brilliant diversity of saleable VAPs that microalgae are capable of producing, and their potential to infuse the global bioeconomy with a novel source of wealth. The major challenges remaining for the microalgal biorefinery relate to 1) providing stable, bioavailable CO_2 in liquid form to microalgae, and 2) effectively valorizing all biomass fractions to saleable VAPs to offset monetary costs, to achieve an economically competitive biorefinery scheme. These challenges are possible to overcome with synchronized scientific research and governmental investment and incentivization.

10. Conclusions

Reducing CO_2 production and CO_2 capture prior to emission are two options for mitigating climate change without severely disrupting global transport and industrial activity. The world's population is growing swiftly, and industrialization is continuously developing to meet societal demands. Consequently, massive volumes of CO_2 are generated and emitted, especially by the energy and transportation sectors. Governments must work in concert with scientists and industry partners to effect these changes. The first element of emissions control is in regulation of harmful compounds, and establishing legal frameworks which more strictly penalize GHG emissions. The second element is providing incentives for developing and implementing green technologies through subsidies, tax breaks, and investment platforms, in order to ensure consistent, sustainable economic growth of carbon–neutral or -negative technologies and sectors. To encourage this economic advancement while preserving the climate, efficient methods for CO_2 capture must be developed in parallel with industrial partners. Chemical absorption, membrane separation, and physical adsorption techniques are commonly used methods for post-combustion CO_2 capture. The

subsequent condensation and deep ocean or geological storage of the captured CO_2, however, is unsustainable. To reach Paris Agreement targets and achieve global carbon neutrality by 2045, this captured carbon must be utilized rather than buried. Several chemical, electrochemical, and photochemical reactions have been tested to convert CO_2 into fine chemicals; these chemical-based reactions, however, are conducted at high temperatures and pressures with highly purified CO_2. The energetic and fiscal costs of these methods are likewise unsustainable. As established by this review, the most feasible pathway to carbon–neutral practices is bio-CCU by photosynthetic microalgae; nature's own carbon capture and upgrading factories made exquisitely efficient by billions of years of evolution. The carbon capture mechanisms evolved over time are capable of highly effective CO_2 sequestration, even at low CO_2 concentrations. Microalgae are likewise adept at upgrading CO_2 into valuable biomolecules, which offer great potential for offsetting the operational costs of microalgal cultivation for CO_2 capture. The microalgal bio-CCU pathway is feasible, sustainable, and profitable, and should universally applied to confront the global peril of climate change.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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