

Chapter 2

Post-combustion Carbon Capture, Storage, and Utilization

Abstract Deployment of carbon capture, storage, and utilization technologies worldwide from the CO₂ emission point source is a strategy that has been proposed to address the challenge of climate change and global warming. As a viable option for reducing CO₂ emissions, moving carbon capture and storage technology to incorporate “utilization” (carbon capture and utilization) has received dramatically global attention. This chapter provides an overview of various types of carbon capture, storage, and utilization technologies. After that, one of the carbon capture and utilization technologies, i.e., microalgae pond systems, is illustrated in detail. The principles of microalgae open pond systems, key parameters affecting productivity, and economic considerations of operating open ponds are systematically illustrated.

2.1 Significance and Importance

Human activities resulted in emissions of four long-lived greenhouse gases (GHGs): CO₂, CH₄, N₂O, and halocarbons, of which CO₂ is the most important anthropogenic GHG due to its solitary responsibility for about two-thirds of the enhanced greenhouse effect [1]. Meanwhile, rapid economic growth in developing countries such as China and India is driving worldwide energy demand and usage day by day. At the same time, it has been predicted that fossil fuels will remain the dominant energy source around the world for at least another 20 years to fulfill such energy demands [2]. As CO₂ keeps accumulating in the atmosphere after generating from power plant, concerns about serious and irreversible damage, such as rising water level and species extinction, are being raised regarding its influence on climate change. Consequently, it is clear that effective control of CO₂ emissions is required to achieve the goal of global CO₂ concentration below 550 ppm over next the 100 years [3].

2.1.1 Strategies on Global CO₂ Mitigation

It is noted that the increased global average CO₂ concentration in the atmosphere is likely to cause further warming and induce many changes in the global climate system. To reduce CO₂ in the atmosphere, five strategies can be considerable [4]:

- Strategy 1: Reducing the amount of CO₂ producer sources (reducing energy intensity)
- Strategy 2: Using CO₂ (or reducing carbon intensity)
- Strategy 3: Capturing and storing of CO₂
- Strategy 4: Switching to less carbon-intensive fuels from conventional fuels
- Strategy 5: Increasing the use of renewable energies.

The third strategy involves the development of innovative, available, and cost-effective carbon capture and storage (CCS) technologies because of a 50-year estimate for the continued widespread burning of fossil fuels, the goal of reaching a 500 ppm atmospheric CO₂ concentration plateau, and the lag time needed for the development and implementation of new carbonless sources of energy [4, 5]. In general, the carbon capture technologies can be classified into three categories:

- Precombustion capture
- Post-combustion capture
- Oxy-fuel combustion

2.1.2 Transition from Storage to Utilization

As a viable option for reducing CO₂ emissions, moving CCS technology to incorporate “utilization” [i.e., carbon capture and utilization (CCU)] has received dramatically global attention. Europe (in particular Germany), the USA, and Australia are well advanced in research and development of carbon capture, utilization, and storage (CCUS) technologies [6, 7]. The utilization routes of the captured CO₂ include enhanced fuel recovery (i.e., enhanced oil recovery and enhanced gas recovery), biological conversion (i.e., algae), food industry, chemicals (i.e., fertilizer and liquid fuel), refrigerant, inerting agents, fire suppression, plastics, and even mineralization as carbonates (i.e., precipitated calcium carbonates (PCC) and construction materials). The benefits of CCU technologies include the following: [6, 8].

- Potentially reduce annual CO₂ emissions by at least 3.7 Gt, equivalent to about 10% of the world’s current annual emissions
- Value-added products that create green jobs and economic benefits and help offset the abatement cost.

As a result, CCUS technologies are key strategies to attenuate the impacts of global warming during the transition period for developing sustainable energy technologies. CCUS is considered to be a critical strategy in the pathway to a sustainable energy system, contributing ~14% of reductions in global CO₂ emissions by 2050 [9, 10]. However, none of the CCUS technologies alone can provide a short—to medium-term solution to reduce CO₂ emissions at a level necessary to stabilize current concentrations. Rather, a portfolio solution must be identified to achieve the most effective CO₂ reduction while minimizing social and economic costs.

2.1.3 Concept of Carbon Capture, Utilization, and Storage (CCUS)

Figure 2.1 shows the major CCUS technologies, including CO₂ capture, storage (sequestration), utilization (direct use), and conversion into chemicals and/or fuels.

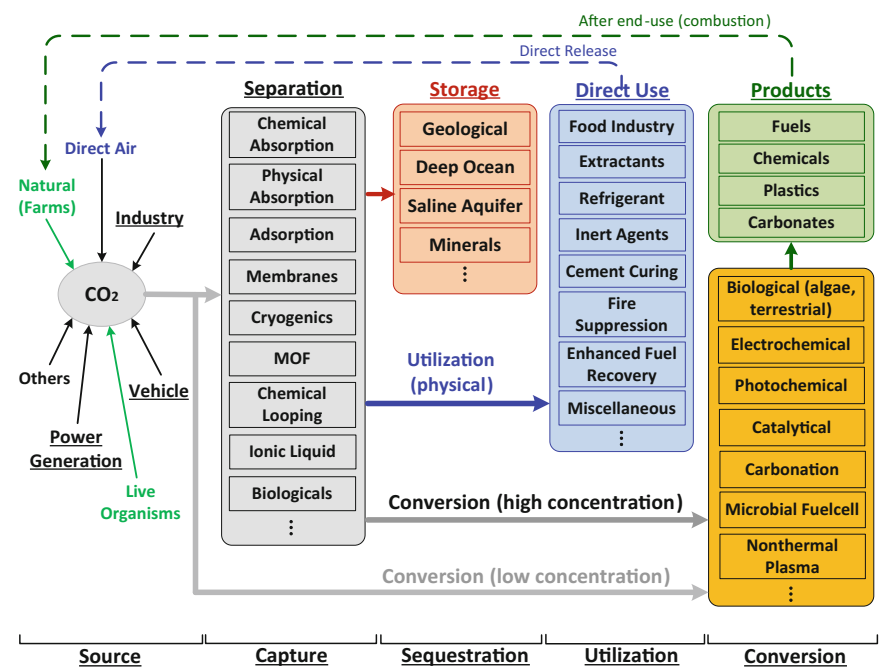


Fig. 2.1 Concepts of post-combustion carbon capture, utilization, and storage (CCUS) technologies

For example, the CCS technologies can effectively capture CO_2 from emission sources, transport it, and then store it at suitable and permanent geological sites.

2.2 Post-combustion Carbon Capture and Storage

As the first step for CO_2 capture, dilute CO_2 in flue gas from industries and/or conventional power plants should be separated and concentrated to a high purity in a cost-effective manner with low energy consumptions. After capture, the CO_2 can be stored into geological or saline formations to ensure long-term sequestration. Also, the concentrated CO_2 stream can be directly utilized or converted into carbon-based materials, such as fuels and chemicals.

2.2.1 Post-combustion CO_2 Capture Technologies

Figure 2.2 shows various approaches to post-combustion CO_2 capture from flue gas or air. Although various CO_2 capture technologies are available, only a few processes have been deployed on a large scale due to significant mass transfer limitations in the processes and the need to treat a significant amount of flue gas [11]. Therefore, successful development and deployment of CO_2 capture processes have been required for obtaining the breakthroughs in innovative reactor concepts and process schemes as well as advancement for new materials.

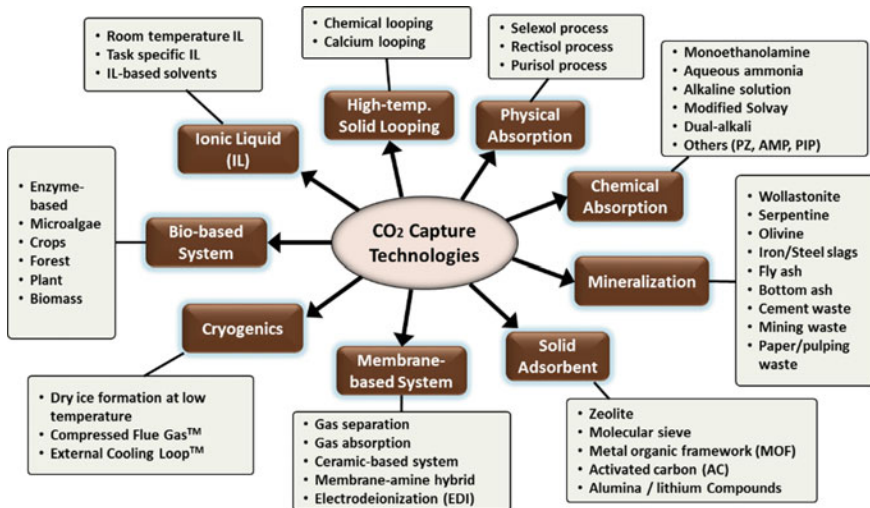


Fig. 2.2 Different approaches to CO_2 capture technologies

In order to achieve the above goals, the dilute CO₂ in flue gas (or air) can be concentrated via various technologies:

- Chemical absorption: alkaline solutions such as NaCl, ammonium solution, and monoethanolamine [11, 12]
- Physical adsorption: zeolite [13], activated carbon [14], and metal-organic frameworks [15]
- Selective membrane separation [16, 17]
- Cryogenic techniques [18]
- Ionic liquid absorption process [19]
- High-temperature solid looping processes: calcium looping [20] and chemical looping [21].

The aforementioned capture technologies can concentrate the dilute CO₂ in flue gas to nearly pure CO₂. After that, it should take the sequential storage or utilization into consideration. Other approaches of post-combustion capture are integrated with CO₂ utilization including the following:

- Mineral carbonation: natural ores and/or solid wastes [22]
- Biological method: microalgae and enzyme-based processes [23].

Some of the CO₂ capture technologies, such as biological method and mineral carbonation, are related to direct conversion and utilization of CO₂ because the physico-chemical property of CO₂ is changed after capture process. Therefore, no additional CO₂ storage site is required with the capture plant. These two approaches, i.e., biological method and mineral carbonation, are illustrated in detail in the following Sect. 2.4 and Chap. 3, respectively.

2.2.1.1 Absorption and Adsorption Processes

Table 2.1 presents the comparison of the post-combustion CO₂ capture technologies by absorption process, such as using aqueous absorbents and ionic liquid (IL). Meanwhile, chemical absorption via aqueous alkanolamine solutions is regarded as the most applicable technology for CO₂ capture by 2030 [24]. It can be accomplished in two stages: (1) CO₂ absorption using an absorbent or solvent, and followed by (2) desorption using pressure, temperature, or electric swing. However, several technological issues, including equipment corrosion, energy consumption in regeneration, and absorber volume, should be critically assessed in using alkanolamine aqueous solutions as absorbents. Thus, a modification and intensification of the absorption process should be considered to enhance the mass transfer between CO₂ gas and solution, for example, a high-gravity rotating packed-bed reactor [25, 26]. In addition, appropriate absorbent genomes, such as using piperazine with diethylenetriamine [27], piperazine with diethylene glycol [28], and NaOH solution [12], are needed to achieve high CO₂ capture efficiency and low regeneration energy.

Table 2.1 Merits and demerits of various physical and chemical absorption processes for post-combustion CO₂ capture

Process description/chemical components		Advantages	Disadvantages
Physical	<ul style="list-style-type: none"> • Selexol process • Rectisol process • Purisol process 	<ul style="list-style-type: none"> • Low vapor pressure and toxicity (Selexol) • Low corrosion (Rectisol) • Low energy consumption (Purisol) 	<ul style="list-style-type: none"> • Low absorption capacity • Limited refractory life (Selexol) • High capital and operating costs (Rectisol)
Chemical	<ul style="list-style-type: none"> • Alkanolamine solution (MEA, DEA, and MDEA) • Sterically hindered amine (AMP) • Promoter (PZ, PIP) 	<ul style="list-style-type: none"> • High absorption capacity • Low operating pressure and temperature • Suitable for retrofitting of the existing power plant 	<ul style="list-style-type: none"> • Severe equipment corrosion rate • High energy consumption in regeneration • Large absorber volume required • Amine degradation by SO₂, NO₂, and O₂
	<ul style="list-style-type: none"> • Ionic liquid (IL) 	<ul style="list-style-type: none"> • Low vapor pressure • Non-toxicity • Good thermal stability • High polarity 	<ul style="list-style-type: none"> • High viscosity • High energy requirement for regeneration • High unit costs

Table 2.2 presents the post-combustion CO₂ capture technologies by adsorption process using solid adsorbent and metal-organic frameworks (MOFs). The adsorption processes exhibit a lower CO₂ adsorption capacity, compared to chemical absorption processes.

2.2.1.2 Chemical Looping Process

Chemical looping process (CLP) is an advanced combustion process, where CO₂ is inherently separated from the other flue gas components. Oxygen-carrier materials, such as Fe-, Cu-, Ni-, Mn-, and Co-based metal oxides, are frequently used in the transfer of oxygen from combustion air to the fuel. In this case, direct contact between fuel and air can be avoided, thereby resulting in near 100% CO₂ in flue gas. Figure 2.3 shows the schematic diagram of CLP for power generation. Oxygen-carrier material (Me_xO_y) is reduced by carbonaceous fuel, such as coal and CH₄, to generate H₂O and CO₂ in the fuel reactor, as described in Eq. (2.1).

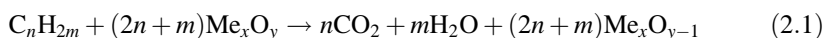
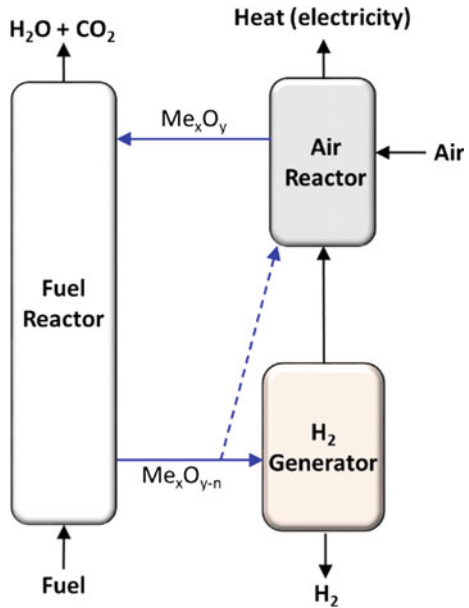


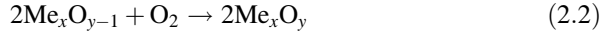
Table 2.2 Post-combustion CO₂ capture processes via physical and chemical adsorption

Process description		Advantages	Disadvantages
Physical	<ul style="list-style-type: none">Activated carbon (AC)ZeoliteMesoporous silica (MS)Metal-organic frameworks (MOFs)	<ul style="list-style-type: none">Wide availability and low costHigh thermal stability (AC)Low sensitivity to moisture (AC)High pore size and tunable pore size (MS and MOFs)	<ul style="list-style-type: none">Low CO₂ adsorption capacityLow CO₂ selectivitySlow adsorption kineticsThermal, chemical, and mechanical stability in cycling
	<ul style="list-style-type: none">Amine-based adsorbentAlkali earth metal adsorbentLithium-based adsorbent	<ul style="list-style-type: none">Exothermic reactionHigh adsorption capacityLow cost in natural minerals	<ul style="list-style-type: none">Deactivation of synthesis adsorbentLow CO₂ selectivitySerious diffusion resistance
Chemical	<ul style="list-style-type: none">Alkaline solid waste (steelmaking slag, ashes, etc)	<ul style="list-style-type: none">Thermodynamically stable productHigh availability of wastesReuse product in a variety of applicationDecreased leaching of heavy metal trace elements from the wastes	<ul style="list-style-type: none">Low CO₂ adsorption capacitySlow adsorption kinetics and mass transferHigh energy consumption in crushing

Fig. 2.3 Schematic diagram of chemical looping process (CLP) for power generation with high-purity CO₂ production



The reduced metal oxide ($\text{Me}_x\text{O}_{y-n}$) is then oxidized to Me_xO_y by oxygen in the air reactor, as expressed in Eq. (2.2), which is an exothermic reaction that provides heat to external facilities, such as electricity generator.



In order to optimize CO_2 production, several challenges in commercialization of CLP still need to be addressed: (1) development of a low-cost oxygen carrier with high reactivity and recyclability; and (2) optimization of reactor design and operating condition. The reactivity of Ni- and Cu-based oxygen carriers is great for chemical looping process; however, their development is still limited due to their high fabrication cost [21]. Regarding the scale of CO_2 capture capacity, CLP has been successfully demonstrated in actual operation in a size of 0.3–1 MW and should be ready to further scale up to the size range of 1–10 MW [29].

2.2.2 Carbon Storage Technologies

The concentrated CO_2 can be pressurized and stored in geological formations underground, so-called geological CO_2 storage, such as

- Deep ocean [30]
- Saline aquifers [31, 32]
- Unminable coal beds [33]
- Depleted oil/gas reservoirs [34]

With widespread geographic distribution, CO_2 (high purity after capture process) injection into confined geological formations can offer a potentially large storage capacity [35]. In general, four major mechanisms for geological CO_2 storage are as follows:

- Dynamic fluid trapping
- Dissolution trapping
- Residual trapping
- Mineral trapping

From the technological point of view, the risks of geological CO_2 storage may include the following [36]:

- Long-term containment risks: potential leakage and induced seismicity
- Site performance risks: improper analysis of wellbore, near-wellbore, and reservoir factors

A nanofluid-based supercritical CO_2 technique could be effectively used for geological CO_2 storage since nanofluids can not only enhance homogeneous CO_2 transport in reservoir but also mitigate the adverse effects of stratigraphic heterogeneity on migration and accumulation of CO_2 plume [32]. Regarding the reaction

mechanism, extensive studies have been carried out to evaluate changes in host rock properties when exposed to CO_2 [37]. A large-scale commercial storage should be conducted with potential exploration of geothermal resource in deep-seated hot rocks. Successful CO_2 sequestration in geological formations, on the one hand, requires a cross-disciplinary effort in geochemical, mineralogical, and petrophysical properties of reservoir and seal materials from the microscopic to the macroscopic scales. On the other hand, prediction and regular monitoring of storage capacity, CO_2 migration and phase state, and long-term reservoir behavior are crucial to ensure the safety, security and sustainability of CO_2 sequestration.

2.2.3 Large-Scale Demonstration Plans

The “utilization” of CO_2 through physical, chemical, or enhanced biological methods should result in effective reductions in CO_2 emissions toward a sustainable carbon cycle. With the development of innovative utilization processes, direct and indirect environmental benefits are expected regarding (1) the reduction of both CO_2 emissions and fossil fuel extractions, and (2) the substitution of chemicals [2]. However, the widespread deployment of CO_2 capture, storage, and utilization (CCSU) projects has not been achieved due to several barriers including the following:

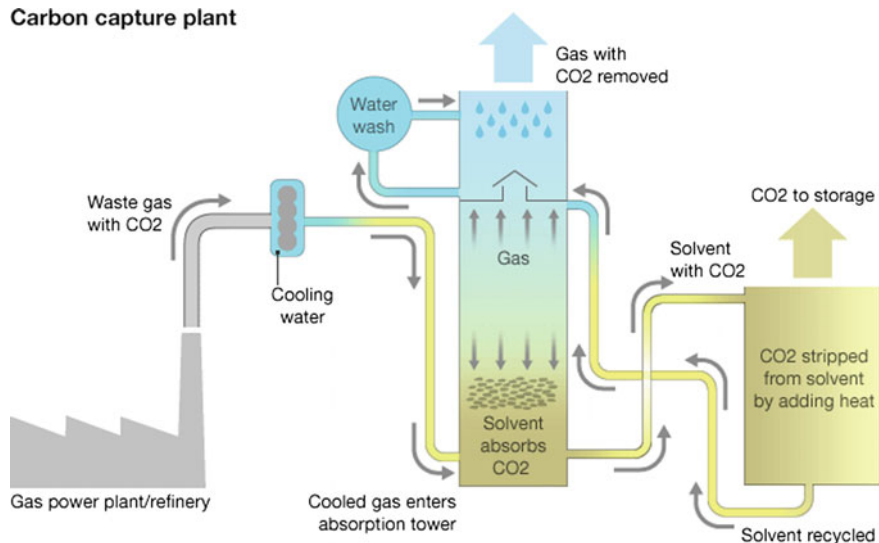
- High capital investment
- Uncertainties in policies, regulations, and technical performance
- Public acceptance
- Concerns about human health and safety
- Environmental risks.

Many countries, such as Norway, Canada, the USA, Germany, and Australia, are advanced in research and development of CCSU technologies [7]. In this section, two large-scale demonstrations in Norway (i.e., CO_2 capture by amine absorption process) and in Canada (i.e., CO_2/SO_2 capture and H_2SO_4 production) are provided and illustrated.

2.2.3.1 Carbon Capture by Amine in Norway (2012)

In Norway, the carbon tax mechanism has been implemented since 1991, thereby leading to the successful development of the first large-scale carbon capture project in the world. As shown in Fig. 2.4, it not only takes CO_2 from a power station but also extracts CO_2 from the natural gas coming from the offshore Sleipner field, owned by Statoil. The efficiency of a modern gas power plant in Norway is typically 59%, such as the one on the southwest coast at Karsto. However, the efficiency would drop to around 50%, if the CO_2 capture unit (including transportation of the CO_2) is installed. Usually, it requires energy to drive the CO_2 capture and

Carbon capture plant



Source: TCM

Fig. 2.4 Schematic diagram of the carbon capture plant by amine in Norway. Reproduced from Ref. [38] by permission of Technology Centre Mongstad (TCM)

storage processes. Therefore, the power station must burn more fuel to produce the same amount of electricity.

In Dong Energy's power station, the CO₂ concentration in the flue gas is about 3%, while the pipe from the cracker at Statoil's Mongstad refinery comes in at around 13%. After absorption process, approximately 90% of CO₂ in the flue gas can be captured. The liquid surface in the absorption tower is estimated to be the same as eight soccer fields.

2.2.3.2 Sask Power Plant in Canada (2015): CO₂/SO₂ Capture and H₂SO₄ Production

At Canada, the Boundary Dam power station (Unit 3), operated by the SaskPower team, has integrated with a carbon capture plant. The project transformed the aging Unit #3 at Boundary Dam power station near Estevan, Saskatchewan, into a reliable, long-term producer of up to 115 megawatts (MW) of base load electricity. The captured CO₂ could be compressed and permanently stored underground (~3.4 km deep), or be liquidized and transported by pipeline to nearby oil company for further utilization, e.g., enhanced oil recovery.

In addition to CO₂, other by-products could be produced from the project. For instance, SO₂ can be captured and converted to sulfuric acid (H₂SO₄) for industrial use. Fly ash, another by-product of coal combustion, could also be sold for use in ready-mix concrete, precast structures, and concrete products. The designed CO₂

and SO_2 emission reduction are 90 and 100%, respectively. In this case, one million tonnes of CO_2 could be captured each year, equivalent of taking more than 250,000 cars off Saskatchewan roads annually.

2.3 Carbon Utilization and Valorization

The most valuable perspective in CO_2 utilization and valorization is not the amount of CO_2 used, since the fixed CO_2 would be reformed within a short time after a CO_2 -made chemical is used. Rather, it is the introduction of innovative technologies for cleaner production that could reduce the use of materials and energy. Carbon utilization and valorisation can achieve a real carbon cycle toward environmental sustainability. After CO_2 capture process, the concentrated CO_2 can be either utilized directly, or converted and transformed into other products, as shown in Fig. 2.5.

In this section, two approaches to utilizing concentrated CO_2 , i.e., (1) direct utilization and (2) conversion and transformation, are briefly illustrated.

2.3.1 Direct Utilization of Concentrated CO_2

Direct use of CO_2 involves phase changes (i.e., states of matter) between gas, liquid, solid, and supercritical fluid. In this case, the concentrated CO_2 can be directly applied in various fields such as [39].

- Food industry
- Soft drinks
- Fire extinguishers
- Extractants
- Solvents for reactions, separation, synthesis, and modification of material: supercritical CO_2 .

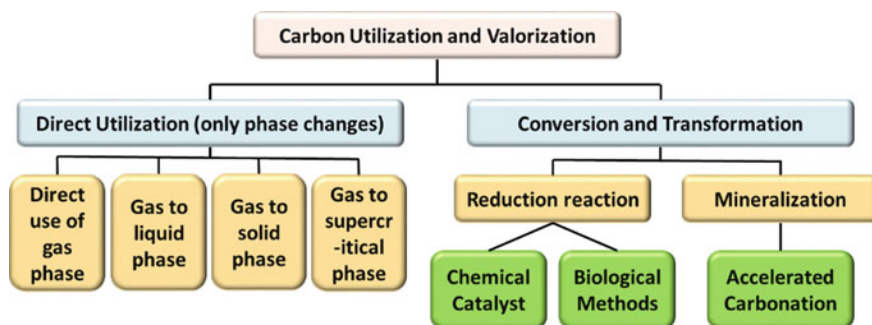


Fig. 2.5 Various approaches to CO_2 utilization and valorization toward sustainable carbon cycle

The economics of the CO₂ utilization technology reply on the quality of CO₂ output (e.g., purity, temperature, and pressure) and the capture processes involved. Currently, the market scales of such applications are still small, which cannot contribute to a huge impact on the overall CO₂ emission mitigation. Moreover, there is a large difference of predicted CO₂ price between the studies. The most acceptable estimate is that the CO₂ price in 2050 might be in the range of 100–400 US \$ per ton CO₂ [40].

2.3.2 CO₂ Conversion and Transformation

Conversion of the captured CO₂ to useful products is an essential strategy toward a sustainable carbon cycle. As CO₂ is a thermodynamically stable compound, conversion of CO₂ typically goes through a catalytic process with additional work input, e.g., renewable energy source. Among the carbon-species compounds, the CO₂ molecule exhibits the highest oxidation state (4+). For this reason, CO₂ conversion and transformation can be realized by.

- Reduction reaction [41]: to a negative-going oxidation state.
- Mineralization [42]: to a lower Gibbs free energy, compared to gaseous CO₂.

Extensive efforts have been underway to increase the CO₂ conversion efficiency under various novel processes. The CO₂ reduction reaction can be achieved by several different approaches, such as electrocatalytic [43, 44], photocatalytic [41], and biological [23] methods. It can not only reduce CO₂ accumulations in the atmosphere but also use CO₂ for furnishing chemicals and energy products. In the following content, the reduction reaction of CO₂ via either chemical catalyst or biological method is provided. The mineralization of CO₂ will be discussed in detail in Chap. 3.

2.3.2.1 Chemical and Catalytic Reaction

The CO₂ can be converted into numerous value-added chemicals via several methods, such as thermochemical, electrochemical, photoelectrochemical, and photocatalytic. In chemical catalytic systems, semiconducting (e.g., TiO₂ and CdS) and/or metal-organic complex materials are commonly used as an additional substance called a catalyst. With the catalyst, reduction reactions of CO₂ occur faster since they require less activation energy. As shown in Fig. 2.6, numerous chemicals (e.g., methane, ethanol, and polymers) can be produced from CO₂ reduction reaction using catalyst.

It is noted that some of the catalytic reduction reactions require the participation of hydrogen (H₂) or proton (H⁺). For this reason, the H₂ (or proton) can be produced from water using exclusively renewable energy, which has been considered

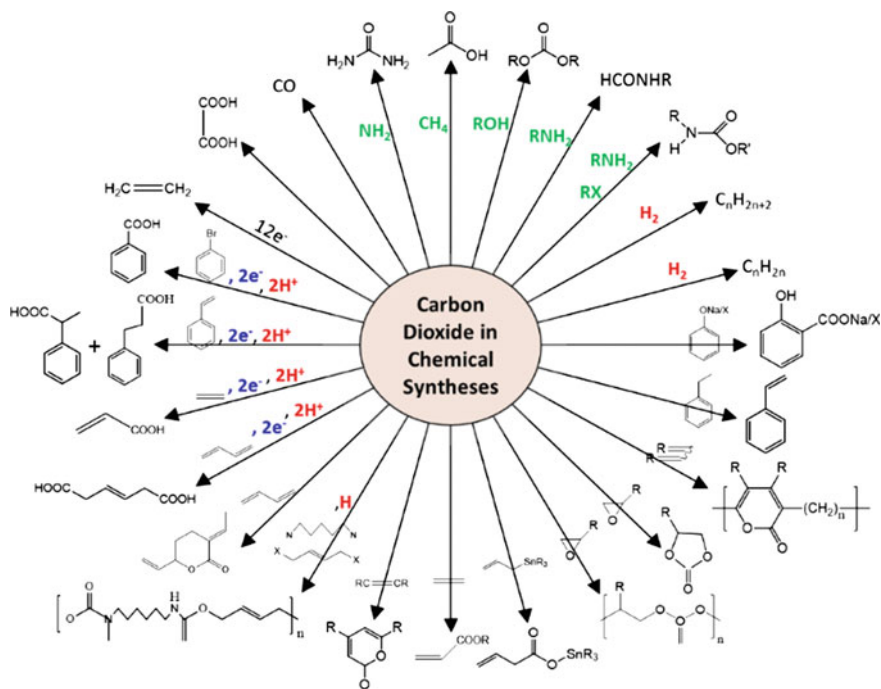
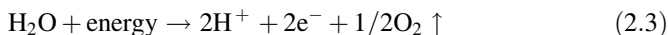
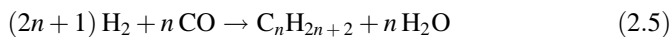
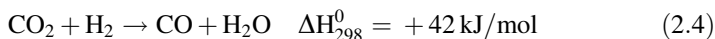


Fig. 2.6 Plentifully potential uses of CO₂ as chemicals through various conversion technologies

as an alternative to store intermittent energy. In electrochemical process, the protons and electrons could be generated from water in an anode compartment using electricity from renewable energy [45], as shown in Eq. (2.3):



The concept of using CO₂ and H₂ to produce chemical fuels, such as methane, methanol, and dimethyl ether (DME), is so-called the production of sustainable organic fuel for transport (SOFT). The CO₂ and H₂ can be converted into liquid hydrocarbon through a combination of the reverse water–gas shift (RWGS) reaction and Fischer–Tropsch (FT) process, as shown in Eqs. (2.4) and (2.5), respectively.



where n is typically ranged from 10 to 20. The FT synthesis involves a series of chemical reaction that produce a variety of hydrocarbons (C_{*n*}H_{2*n*+2}).

On the other hand, the CO_2 and H_2 can be converted into, for instance, methanol via Eq. (2.6):



The key to successful SOFT production relies on three elements: (1) a cheap source of CO_2 , which depends on the types of CO_2 capture process; (2) a cheap source of H_2 , which may be combined with renewable energy utilization; and (3) an effective and robust catalyst to initiate the reduction reaction. Regarding the catalytic systems, they typically suffer from low efficiency of CO_2 reduction reaction due to several limiting factors [41]:

- Fast electron–hole (e^- - h^+) recombination rates
- Complicated backward reactions
- Low CO_2 affinity of the photocatalyst

2.3.2.2 Enhanced Biological Fixation

Another approach to CO_2 reduction reaction is via the biological methods using fast-growing biomass, called enhanced biological fixation. It corresponds to the production of aquatic and/or terrestrial biomass under non-natural photosynthetic conditions. For instance, direct use of CO_2 by “microalgae” has attracted great interest since microalgae can not only consume CO_2 but also be converted to biochemicals or biofuels. Microalgal cells are sunlight-driven cell factories that can convert CO_2 into raw materials for producing biofuels (or solar fuels), animal food chemicals, and high-value bioactive compounds such as docosahexaenoic acid [46]. The reaction can be achieved by two separate mechanisms:

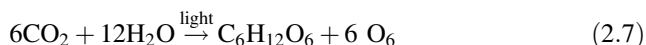
- Light-dependent set: Solar light (uv) energy is used to excite electrons for reducing the coenzyme NADP^+ to NADPH and creating the high-energy molecule ATP.
- Light-independent set: The reduced molecules are utilized to convert CO_2 to organic compounds that can be used as a source of energy by algae.

Due to its carbon neutral property, the production of bio-based chemicals in biorefineries using biomass is a key opportunity for sustainable green growth. Based on a cradle-to-grave life cycle assessment [47], bioproducts could provide reductions of 39–86% in greenhouse gas emissions, compared to their fossil counterparts. Furthermore, the reaction products, such as biochemicals, may offer a high added value, providing an opportunity to cover the costs of biomass production (e.g., algal). Biotechnologies are expected to contribute to 2.7% of GDP in 2030 within the OECD region and make the largest economic contribution in

industry and primary production [48]. As a result, the biological process for CO₂ utilization and transformation should be feasible from an economic standpoint and acceptable from an energy perspective.

2.4 Case Study: Microalgae Pond for CO₂ Capture and Utilization

Algal technology offers great potential to combat the global energy and CO₂ crisis and malnutrition, while also generating high value-added products. Microalgae have been recognized as an alternative feedstock to energy conversion and/or chemicals production. They are fast-growing and ubiquitous photosynthetic organisms, which are rich in protein and chemical compounds, and can be converted to biodiesel fuel using a variety of different methods. Microalgae have been recognized as a third-generation source of biofuels not only because they use CO₂ from the atmosphere, as indicated in Eq. (2.7), but also due to their high lipid content per biomass compared to other plants [49].



Microalgae are superior to terrestrial energy crops, in terms of biomass and biodiesel yield [50]:

- Microalgae in photobioreactors: ~150 Mt/ (ha-year)
- Microalgae in open ponds: 50–70 Mt/ (ha-year)
- Switch grass (terrestrial): ~13 Mt/ (ha-year)
- Corn (terrestrial): ~9 Mt/ (ha-year)
- Soybeans (terrestrial): ~3 Mt/ (ha-year).

Microalgae can be used as a feedstock for manufacturing a number of products:

- Bioenergy: biodiesel, biogas, bioethanol, etc.
- Non-energy bioproducts: carbohydrates, pigments, protein, biomaterials, etc.
- Animal feed.

As a result, microalgae could provide huge market potential for biodiesel as well as other valuable biochemicals. However, since the productivity (or yields) of the bioproducts has certain stoichiometric and thermodynamic constraints (fundamental principles of biochemistry), the maximum theoretical energy conversion of the full sunlight spectrum into organic matter is about 10% [49]. Aside from stoichiometric and thermodynamic constraints, algal cultivation is considered as one of the technological barriers. It is noted that algal cultivation accounts for one-third of the total cost involved in the algal biofuel production process [51].

In the following section, the types of open pond systems and the key parameters affecting productivity for the microalgae cultivation as well as the process economics are discussed.

2.4.1 Types of Open Pond Systems

For algal cultivation, the open ponds are easier to construct and operate than most closed systems, thereby resulting in low production costs and low operating costs. Four major open pond systems can be used for algal cultivation:

- Shallow big ponds
- Tanks
- Circular ponds
- Raceway ponds.

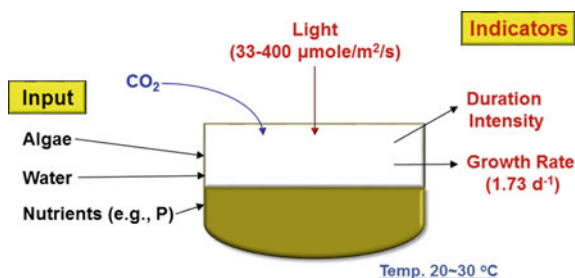
Since each of them exhibits its own characteristic features, the selection of an appropriate open ponds for cultivation relies on the types of algal species, location of plant installation, local climatic conditions, and cost of water and lands [52]. Figure 2.7 shows the schematic diagram of material flows in an open pond system. Microalgae require the same basic element inputs as plants, including light, CO_2 , water, and inorganic nutrients (such as P compounds). As a result, environmental factors such as light intensity, temperature, pCO_2 , PO_2 , pH, and salinity play a crucial role in microalgae productivity. During algal growth, the chlorophyll- α content, algae cell density, DO, and pH of the solution can grow rapidly.

In general, open ponds can offer greater CO_2 fixation capacity than tubular reactors due to their greater culture volume per area [53]:

- Open ponds: $100\text{--}300 \text{ L-CO}_2/\text{m}^2$
- Tubular reactors (1–5-cm tubes): $8\text{--}40 \text{ L-CO}_2/\text{m}^2$.

Production of microalgae in raceway ponds is considered the most promising technology for algal cultivation, especially in the large scale [51]. Typically, the surface-to-volume ratio of raceway ponds (i.e., the depth of pond) is approximately $5\text{--}10 \text{ m}^{-1}$ [54]. The shallow configuration is required for raceway ponds to prevent

Fig. 2.7 Schematic diagram of material flows in an open pond system



light limitation inside the culture, thereby resulting in a linear land footprint when it comes to scale-up. In addition, typical process hurdles for raceway ponds still may include the following: [55].

- High risk of culture contamination from strains of bacteria or other outside organisms
- Lack of temperature control (or environment condition control due to weather)
- Inefficient stirring mechanisms
- Poor gas–liquid mass transfer
- Low final biomass concentrations incurring high harvesting costs

2.4.2 Key Parameters Affecting Productivity

Numerous external and internal factors will significantly affect algal growth and productivity in the open pond systems, including the following:

- Environmental factors: location of the cultivation system, rainfall, solar radiation, etc.
- Engineering factors: pond depth, CO₂ delivery system, methods of mixing, power consumption, etc.
- Biological factors: light, pH, oxygen accumulation, salinity, algal predators, etc.

Table 2.3 presents the aforementioned factors affecting algal growth, biomass accumulation, and production for most algae in open ponds. Normally, the most challenging and important factors discussed in photobioreactor design and operation are sufficient mixing (stirring), rapid carbon utilization, and the accumulation of photosynthetically produced oxygen [53]. Therefore, controlling pH, conductivity, and O₂ concentration of the culture is important to obtain a high biomass concentration and productivity [56]. It was noted that an excess of both pH and dissolved O₂ in ponds would significantly reduce biomass concentration and productivity, especially in mid-summer, while no inhibition of growth by excess irradiance and temperature is expected [56].

In the following section, several important factors, including (1) light (radiation), (2) temperature, (3) mixing, (4) CO₂ delivery and cultural pH control, (5) accumulation of dissolved oxygen, and (6) salinity, are discussed.

2.4.2.1 Light (Radiation)

Light (or photolight uv) is essential for algal growth since the growth of all algal species is highly dependent on solar radiation of the pond or water body. It suggests that maximum algal growth rate should be obtained at the light saturation (irradiation) point. Beyond the light saturation point, algal growth would be inhibited because of the photoinhibition mechanism. The photoinhibition is a series of

Table 2.3 Significant factors affecting algal growth, biomass accumulation, and production for most of algae in open pond system. Reprinted by permission from Taiwan Association for Aerosol Research: Ref. [80], copyright 2016

Categories	Factors	Influence (features)	Rule of thumb	Reference
Environmental (location)	Irradiance (light intensity)	Algae growth	Minimum of 4.65 kWh m ⁻² d ⁻¹	[57]
	Rainfall	Chance of culture dilution	Not more than 1 m per year	[58]
	Land slope	Earth-moving costs during pond construction	Not more than 5%	[59]
	Contiguous area	Ensure a commercial scale (i.e., 3.8 dam ³ y ⁻¹ of oil feedstock)	Minimum 3.2–10.5 km ²	[58]
Engineering	Pond depth	Temperature, light utilization efficiency, mixing, and power consumption of mixing, etc.	Typical 15–20 cm (raceway)	[23]
			Typical 20–30 cm	[60]
			Productivity increased 134–200% in depth of 40 cm (compared to 20 cm)	[61]
	Mixing	Light utilization efficiency, oxygen removal rate, etc.	Kept between 5 and 30 cm s ⁻¹	[51]
	CO ₂ delivery system	Affected by diffusor	At least 65 μmol L ⁻¹	[53]
	Power consumption	Affected by water head and types of paddle wheel	Typical 1.5–8.4 W m ⁻³	[62]
Biological	Light (wavelength, photoperiod)	Autotrophic growth and photosynthetic activity	400–500 nm (for chlorophyll a, chlorophyll b, and carotenoids)	[63]
	Biomass concentration (areal density)	Pigmentation to block light	Up to 0.66 g L ⁻¹	[64]
	pH	CO ₂ concentration in the culture	Optimal in the range of 7–8, no more than 8.5	[53, 65]
	Oxygen accumulation	Results in photooxidation and respiration of cell	Not more than 25 mg L ⁻¹	[56]
	Salinity	Growth and cell composition of microalgae	Range between 22 and 28 mS cm ⁻¹	[56]
	SO ₂	May not directly inhibit growth but increase acidity	Must below 100 mg/L	[23]
	C:N ratio	Composition in algal cells	Range from 6 to 8	[66]
	Temperature	Cellular chemical composition, uptake of nutrients and CO ₂ , growth rates for every species of algae	Minimal temperature around 18 °C	[67]
			Different optimal temperatures ranging from 24 to 42 °C	[68]
	Nutrient/media (N, P, S)	Growth and composition of benthic algae. Formation of microalgae (CH _{1.7} O _{0.4} N _{0.15} P _{0.0094})	N: 4–8% per dry weight basis algae P: 0.1% per dry weight basis algae S: 0.5% per dry weight basis algae	[60]

complex reactions that inhibit different activities of photosystem II (or water-plastoquinone oxidoreductase). So far, there is no consensus on the real mechanisms of photoinhibition. The photoinhibition can occur at all light intensities, and the rate constant of photoinhibition is directly proportional to light intensity. From the aspect of engineering design, the depth of open ponds is directly dependent on irradiance spectra. The appropriate depth of open pond system can be determined by measuring the irradiance attenuation coefficient as a function of wavelength for each strain [63].

2.4.2.2 Temperature

Temperature maintenance in raceway ponds is challenging and important work. Productivity of microalgae increases as the pond temperature increases up to an optimum temperature. Above the optimum temperature, algal respiration and photorespiration increase, thereby reducing overall productivity. It suggests that the optimum ranges of temperature and light irradiance for growth are 20–30 °C and 33–400 $\mu\text{mol m}^{-2} \text{s}^{-1}$, respectively, for algae species such as [69].

- Most of green algae
 - *Botryococcus*
 - *Chlorella*
 - *Chlamydomonas*
 - *Haematococcus*
 - *Neochloris*
 - *Nannochloropsis*
 - *Scenedesmus*
 - *Spirogyra*
 - *Ulva*
- A few species of brown algae
- A few species of red algae
- A few species of blue-green algae

Similarly, the Algae Raceway Integrated Design (ARID) also suggests that diurnal and seasonal temperature fluctuations should be minimized. The temperature should maintain within the optimal range of 15–30 °C.

2.4.2.3 Mixing

Mixing, especially vertical mixing, is considered the most significant factor affecting the performance of raceway ponds since it is largely related to light utilization efficiency. The importance and significance of sufficient mixing in raceway ponds includes the following [51, 54, 70]:

- Periodic exposure of cells to sunlight
- Keeping cells in suspension
- Availability of the nutrient to algal cells
- Removal of photosynthetically generated dissolved oxygen (DO) to avoid photooxidation and photoinhibition by respiration, thereby enhancing light utilization efficiency

Typically, mixing accounts for $\sim 69\%$ of total utility costs [71]. Therefore, the mixing intensity should be carefully adjusted according to the environmental conditions. For instance, the mixing velocity should be reduced during the night and even in winter time to avoid excess biomass loss in the absence of light.

2.4.2.4 CO₂ Delivery and Effect of Culture PH Value Control

Microalgae can be successfully grown in various types of liquid phases, such as (piggy) wastewater and deep-sea water. Typical, the carbon-to-nitrogen (C:N) ratio in the algal cells ranges from 6 to 8 [66]. When wastewater is used for algae cultivation, additional CO₂ delivery is imperative for maintaining a sufficient carbon source because the C:N ratio of wastewater is generally 3. In high-rate ponds, a supply of concentrated CO₂ greater than 5% is needed to sustain algal growth [72]. CO₂ delivery largely depends on culture pH and the factors affecting mass transfer rates, such as type of sparger, mixing intensity, liquid velocity, and gas–liquid contact time. The rate of CO₂ absorption in the solution increases with an increase in the pH of the solution. For most algae species, the optimal pH ranges from 7 to 8 to maintain sufficient bicarbonate species in the solution [65].

In open ponds, the dissolved CO₂ after recarbonation tends to be desorbed to the atmosphere. It was estimated that the mass transfer coefficient (K_L) for CO₂ release through the surface of a 100-m² pond should be about 0.10 m/h [53]. For the actively growing algal cells, a sufficient CO₂ mass transfer rate should be at a pH value of 8 [73]. In some cases, however, maintaining a pH in the range of 9.5–10.5 (such as *Spirulina* sp.) is necessary to minimize the chances of contamination with other microalgae [56, 66]. As a result, open pond systems should be operated at higher pH and lower alkalinity than tubular reactors.

2.4.2.5 Accumulation of Dissolved Oxygen (DO)

Oxygen (O₂) is a by-product generated from the algal culture in the course of photosynthesis. Stoichiometric analysis revealed that 1.9 g of O₂ would be generated per gram of the algal biomass synthesis [66]. However, a high concentration of dissolved oxygen (DO) during algal cultivation would severely damage the algal cells by photooxidation and inhibit photosynthesis via respiration. The accumulation of DO in the culture thus will lead to a reduction in biomass productivity. It is necessary to maintain sufficient mass transfer by sparging, even when no carbon is required. The energy required for increasing mass transfer rate and reducing DO

concentrations could be compensated by the increased biomass and its associated potential energy yields.

Removal of accumulated DO from microalgae system is a more critical design criterion than other unit processes, such as carbon supply. It is noted that an increase in DO concentration greater than 25 mg/L might exhibit a negative impact on the biomass productivity [56]. At the maximal rate of photosynthesis, a 1-cm tubular reactor would accumulate 8–10 mg O₂/L/min, which may easily result in the O₂ concentrations over 100 mg/L [53]. In contrast, the DO in open ponds rises much more slowly as a consequence of the much greater volume per unit surface area, where the maximum DO concentration is typically 25–40 mg/L [53, 66]. It was estimated that the maximum DO levels for an open pond with a 100-m² surface and a 20-cm depth should be 14.5 mg/L at a mixing velocity of 30 cm/s, or 19.0 mg/L at a mixing velocity of 3.7 cm/s [53].

2.4.2.6 Salinity

In water chemistry, salinity is defined as the saltiness or dissolved salt content of a water body. It is a thermodynamic state variable (along with temperature and pressure), which governs physical characteristics of a water body such as the density and heat capacity. The salinity of the solution would affect the growth and cell composition of microalgae via several mechanisms, including the following: [74].

- Osmotic changes
- Ion (salt) stress
- Changes of the cellular ionic ratios (membrane selective ion permeability)

In open ponds, fluctuation in the salinity of the culture due to evaporation, rain, and precipitation is a common issue, especially with brackish or saline water [51]. The simplest way to solve the fluctuation issue is to add extra freshwater or salt as necessary. Daily refilling with freshwater in open ponds could maintain the conductivity of the culture ranging 22–28 mS cm⁻¹ [56].

Aside from consecutive addition of freshwater, appropriate water treatment and/or separation processes for the culture could be employed to maintain the salinity of the culture. Available treatment technologies for the culture desalting include membrane separation [75]. However, the main challenge in membrane process is the precipitation of calcium salts, especially in calcium-laden water, thereby resulting in loss of alkalinity and other minerals (such as phosphorus and iron) [76].

2.4.3 Economic Considerations

For microalgae technology, the optimal control of pH, conductivity, and O₂ concentration in the culture is extremely important to obtain a high biomass

concentration and productivity. A comprehensive performance evaluation (CPE) among the unit processes is critical to achieve high engineering performance while maintaining low cost and environmental impacts. The most challenging work in assessing the economics of microalgae process are (1) the cost of the CO₂ supply and (2) the uncertain nature of downstream processing [77].

The high cost of CO₂ capture and transportation is the major obstacle for algal biomass production. Therefore, converting CO₂ into a bicarbonate/carbonate aqueous solution is preferred since it can be easily transported in a water pipeline under normal pressure [78]. To achieve the above goal, efficient conversion of CO₂ from a flue gas into aqueous bicarbonate/carbonate solution should be developed, for example,

- Carbonate–bicarbonate buffer [65]
- CO₂ hydrate [79]
- Electrochemical membrane process [75]
- High-gravity rotating packed-bed reactor

On the other hand, regarding the downstream processing, biofuels (e.g., algae-to-fuel technology) should be produced simultaneously with value-added coproducts from the perspective of green economy and green design [49]. Furthermore, integration of an energy-efficient ex situ water treatment process for the culture solution with existing open ponds might be an alternative. In this case, provision of sufficient CO₂ concentration and removal of excess O₂, (in-)organic acid, and salinity from the culture could be simultaneously achieved.

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