

## Recent Advances in Carbon Dioxide Utilization

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### Abstract

Carbon dioxide (CO<sub>2</sub>) is the major contributor to greenhouse gas (GHG) emissions and the main driver of climate change. Currently, CO<sub>2</sub> utilization is increasingly attracting interest in processes like enhanced oil recovery and coal bed methane and it has the potential to be

used in hydraulic fracturing processes, among others. In this review, the latest developments in CO<sub>2</sub> capture, utilization, conversion, and sequestration are examined through a multi-scale perspective. The diverse range of CO<sub>2</sub> utilization applications, including mineralization, biological utilization, food and beverages, energy storage media, and chemicals, is comprehensively presented. We also discuss the worldwide research and development of CO<sub>2</sub> utilization projects. Lastly, we examine the key challenges and issues that must be faced for pilot-scale and industrial applications in the future. This study demonstrates that CO<sub>2</sub> utilization can be a driver for the future development of carbon capture and utilization technologies. However, considering the amount of CO<sub>2</sub> produced globally, even if it can be reduced in the near- to mid-term future, carbon capture and storage will remain the primary strategy and, so, complementary strategies are desirable. Currently, the main CO<sub>2</sub> utilization industry is enhanced oil and gas recovery, but considering the carbon life cycle, these processes still add CO<sub>2</sub> to the atmosphere. In order to implement other CO<sub>2</sub> utilization technologies at a large scale, in addition to their current technical feasibility, their economic and societal viability is critical. Therefore, future efforts should be directed toward reduction of energy penalties and costs, and the introduction of policies and regulation encouraging carbon capture, utilization and storage, and increasing the public acceptance of the strategies in a complementary manner.

**Keywords:** CO<sub>2</sub> utilization; Carbon Capture, Utilization and Sequestration (CCUS); Carbon Capture and Storage (CCS); Climate change

## 1 Introduction

Carbon dioxide (CO<sub>2</sub>), as one of the greenhouse gases (GHGs) emissions emitted by human activities, is the main cause for climate change [1]. As of 2018, global CO<sub>2</sub> emissions had increased to 37.1 Gt, of most of which still comes from the combustion of fossil fuels from a wide range of industrial processes and transportation. Additional increase in anthropogenic CO<sub>2</sub> production in 2019 appears likely due to the sustained use of oil and natural gas and the strong increases projected to drive the worldwide economy [2]. According to data from the National Oceanic and Atmospheric Administration / Earth System Research Laboratory, global CO<sub>2</sub> emissions are steadily increasing, and CO<sub>2</sub> concentration in the atmosphere has reached 411 ppm, a new record high [3]. BP's Energy Outlook claims that CO<sub>2</sub> emissions from energy use will continue to rise through the next several years, increasing by ~10% by 2040 in the evolving transition scenario [4]. In response to these dramatic increases, the Intergovernmental Panel on Climate Change (IPCC) recently recommended limiting global warming to 1.5 °C instead of 2.0 °C to reduce catastrophic climate change issues [5]. In consequence, finding methods to convert CO<sub>2</sub> to useful commodities could spur the development of novel techniques, products, and industries, and help to reduce the climate-altering emissions. Several international agreements have been reached, considering that carbon capture, utilization and sequestration (CCUS)—an integration of carbon capture and utilization (CCU) and carbon capture and storage (CCS)—is essential to cut CO<sub>2</sub> emissions in a sustainable way to limit the severity of climate change [6-8].

In a CCUS process, CO<sub>2</sub> is first captured from exhaust gases of fossil fuel combustion and purified to deliver a high-purity CO<sub>2</sub> stream, after which it can either be sequestered or converted to valuable products with environmental, economic, and social benefits. CO<sub>2</sub> can be physically and chemically employed in the various fields of chemical, biological, and food processes, which are at different stages of development and demonstration.

However, we are drastically failing in meeting our targets of GHG reduction, which can be seen in terms of arctic changes and ocean acidification [9, 10], and we will need every option, including CCS for gas and coal projects, and CCU in the near future to reduce energy and resource consumption, and improve innovation and competitiveness.

Here, we first present the trends and status of research on carbon dioxide utilization (CDU). We review a diverse range of CDU technologies, including mineralization, biological utilization, food and beverages, energy storage, and chemicals production. We also illustrate the current research and development (R&D) CDU projects worldwide. Lastly, we discuss the market, policies, and challenges in CDU, and then propose priority research directions for the future.

## **2 CO<sub>2</sub> Utilization Technologies**

In the CCUS framework, CO<sub>2</sub> is utilized in a variety of ways, mainly mineral carbonation, physical and chemical methods, which are discussed below.

### **2.1 Fuels and Chemicals**

CO<sub>2</sub> can be utilized as a building block, or feedstock for the sustainable production of chemicals or even fuels, providing extra added value and potentially sequestering CO<sub>2</sub> [11]. The common products made from CO<sub>2</sub> include urea, formic acid, methanol, cyclic carbonates, and salicylic acid [12, 13]. Among them, some products such as formic acid should be preferentially considered because they have the largest potential for CO<sub>2</sub> emission reduction [14]. To compete with fossil fuel-derived products, the economic feasibility studies are very important, which consider uncertainties in market due to government policies and legislations (e.g., carbon tax).

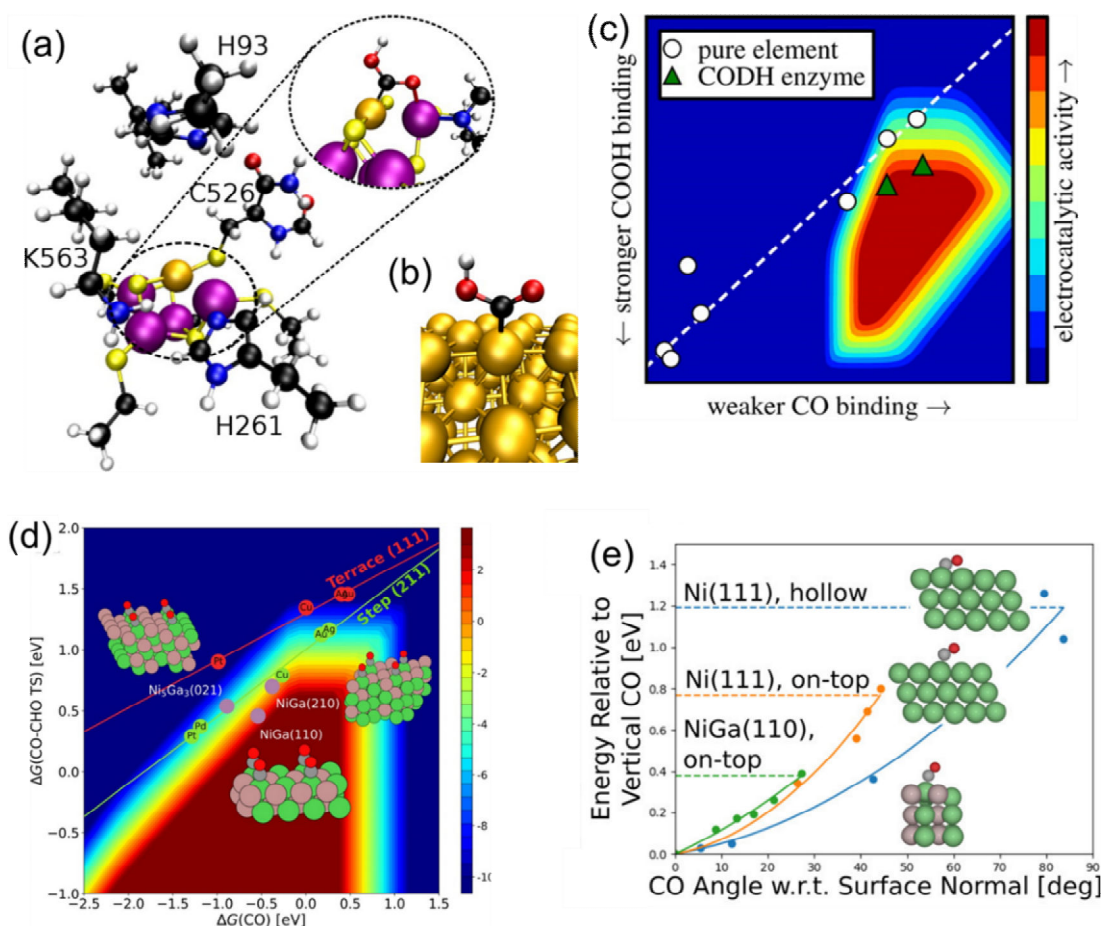
#### **2.1.1 Electro-catalytic conversion**

There are complicated pathways to convert CO<sub>2</sub> into chemicals or fuels including electrochemical, thermocatalytic, photochemical, biochemical, and hybrid methods [15].

Electro-catalytic methods for converting CO<sub>2</sub> to commercially-valued products, including carbon monoxide [16], methane [17], methanol [18], and hydrocarbons [19], have been broadly studied using both experimental and theoretical methods. Liquid-phase electro-catalysis has a relatively complex mechanism, with very different reaction intermediates and final products, and various catalytic systems used. In particular, both heterogeneous metallic catalysts and enzymes have been found to be suitable for such reactions [20]. Here, the catalytic site effect has been shown to be particularly important to ensure selective CO<sub>2</sub> reduction, but usually more easily achieved, compared to the competing hydrogen evolution reaction [21]. The mechanistic insights for Au, Ag and Cu have been elucidated by density functional theory (DFT) calculations, while inactivity of Pt is still not explained. Interestingly, unlike the other metallic catalysts, Cu selectively converts CO<sub>2</sub> to hydrocarbons such as methane and ethylene [22]. Using DFT calculations, Nie *et al.* [23] have suggested a series of possible pathways for the selective CO<sub>2</sub> reduction on Cu. For a rational catalyst design, Hansen *et al.* [24] have developed a volcano-shaped contour plot to describe the trends of the CO<sub>2</sub> electro-reduction, with the CO and COOH<sup>-</sup> adsorption energies as the reaction descriptors (**Fig. 1(a-c)**). With more DFT-calculated thermodynamic parameters, Cheng *et al.* [25] further designed a series of Au- and Ag-based single-atom catalysts (Au or Ag surface atoms replaced by “strong-binding” transition metals) that could theoretically convert CO<sub>2</sub> to hydrocarbons. Ma *et al.* [26] and Ulissi *et al.* [27] used the machine learning method (i.e., artificial neural networks [28]) for a larger-scale catalyst screening of alloy surfaces (**Fig. 1(d)**). Specifically, they evaluated various binding sites on NiGa alloys and found highly active sites (**Fig. 1(e)**). Also, based on the recently developed “tunability” theory of adsorbate (*e.g.*, H and CO) bindings with the atomic ensemble effects, it is expected that some new types of alloy catalysts may be highly active and selective in CO<sub>2</sub> electro-reduction processes. More recently, new catalytic systems have also been evaluated for CO<sub>2</sub> electro-reduction, including graphene and defected graphene [29], nitrogen-doped graphene [30], transition metal sulfides [31],

core@shell materials [32], complexes [33], supramolecular porous organic cages [34], and metallic/oxide nanosheets [35]. These studies have shown that new materials can be applied for CO<sub>2</sub> electro-reduction with relatively high activity, selectivity, and stability. However, the more expensive and exotic the precursor materials are, their use in any particular scheme at an industrial scale is limited.

Although several studies have been reported for CO<sub>2</sub> electro-reduction on catalytic surfaces, there are still challenges that limit further development. These include uncertain kinetic parameters for the various reactions [36], mismatching between current theories and experiments [37], and the formation of unstable metallic structures during catalysis [38]. These issues result mainly from the lack of *in situ* observation on the reaction mechanisms and active sites during experimentation. Though theoretical studies provide insights into the reaction mechanisms and new catalyst design, there are limits in the modeling of the systems. For example, water and solvation effects have been found to be particularly important for mechanistic studies of CO<sub>2</sub> reduction using DFT. However, most previous modeling studies have not considered the presence of water molecules, which leads to higher uncertainty and discrepancies between model predictions and experiments. This not only hinders the rational design of highly active and selective CO<sub>2</sub> reduction catalysts, but also limits the applications of CO<sub>2</sub> electro-reduction in industries. However, they can be addressed with further theoretical studies and *in situ* experiments.

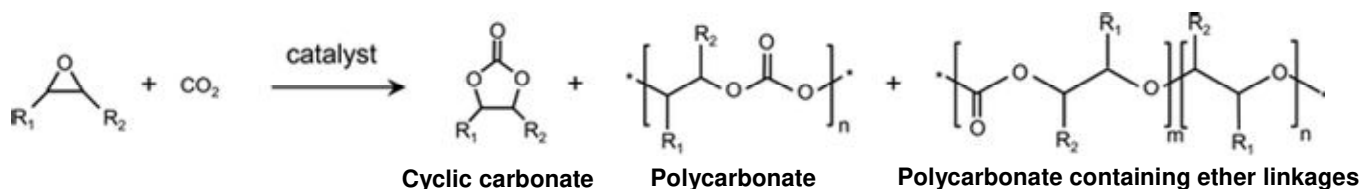


**Fig. 1** Models of the active site for CO<sub>2</sub> electro-catalytic reduction on (a) enzyme and (b) Au surface. (c) Volcano activity plot for CO<sub>2</sub> electro-catalytic reduction at a 0.35 V overpotential. The data were obtained from the (211) stepped sites of transition metals. (d) Predicted activity of transition metal and the NiGa sites. (e) Rotation energy of CO on Ni and NiGa (110). Reprinted with permission from Refs. [24, 26].

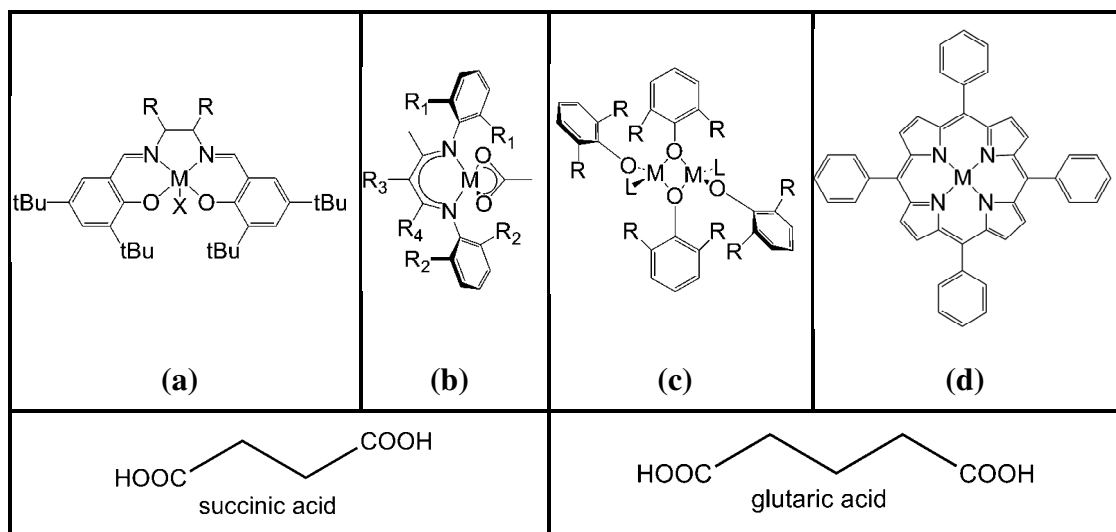
### 2.1.2 Plastics

CO<sub>2</sub>-based polymers used as the raw materials for plastics are potentially more environmentally friendly, and hence have attracted much industrial attention [39]. They are produced by copolymerization of hydrocarbons and CO<sub>2</sub> (about 31-50%), which reduces the consumption of petrochemical products [40]. CO<sub>2</sub> was first used by Inoue *et al.* [41] in 1969 in the sequential copolymerization process with epoxides to form high-molecular-weight aliphatic polycarbonates, as illustrated in **Fig. 2**. Importantly, the polymerization

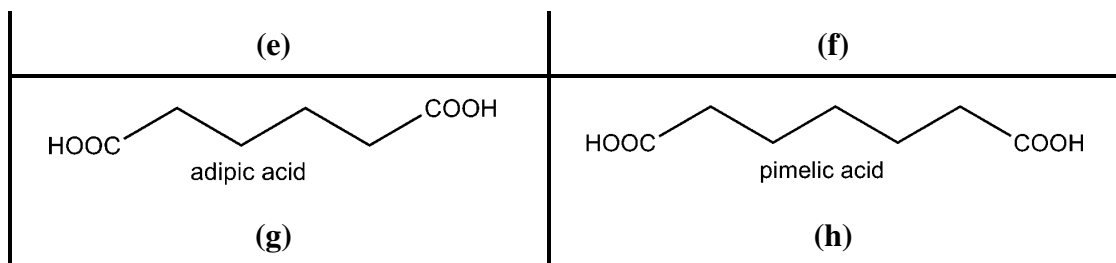
reaction needs to be catalyzed. Therefore, the production of cheap and efficient catalysts is the key to future developments. The commonly used catalysts in the copolymerization between CO<sub>2</sub> and the epoxides include homogeneous, heterogeneous and supported catalysts, and are mainly organometallic compounds [42]. **Fig. 3** shows the representative homogeneous and heterogeneous catalysts for the copolymerization process [40, 43]. Among them,  $\beta$ -diiminate (BDI) zinc complexes [44-46], rare earth metal complexes [47, 48], metalloporphyrin complexes [49], and Schiff-base metal complexes [50, 51] are widely employed in current research. A good copolymerization catalytic system should have high selectivity activity, and be easy to prepare, safe and nontoxic [52]. The large-scale application of CO<sub>2</sub> copolymers is still limited due to relatively low catalytic activity and poor thermal and mechanical properties.



**Fig. 2** Possible products from CO<sub>2</sub> reacting with epoxides. Reprinted with permission from Ref. [53].

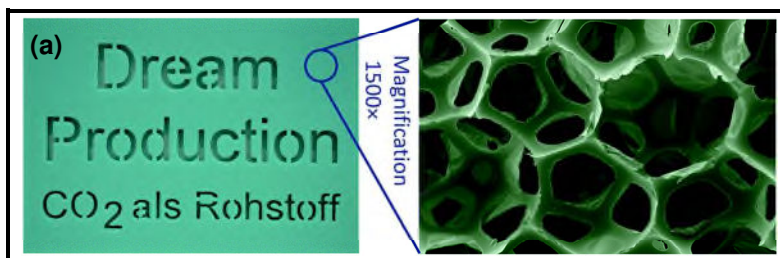


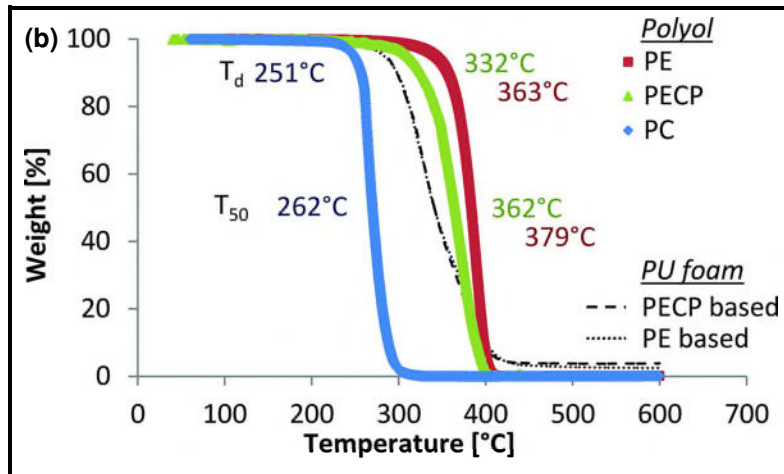




**Fig. 3** Common homogeneous catalyst systems (a) salen, (b)  $\beta$ -diiminate, (c) phenoxides, (d) porphyrin; and acids used in the heterogeneous catalyst synthesis (e) succinic acid (C<sub>4</sub>), (f) glutaric acid (C<sub>5</sub>), (g) adipic acid (C<sub>6</sub>), (h) pimelic acid (C<sub>7</sub>). Reprinted with permission from Ref. [40].

In past decades, there have been a large number of experimental and theoretical studies on the reaction mechanisms, catalytic efficiency, and the applications of polymers [53-57]. Polyoxymethylene (POM) is a polycondensation polymer which can be fabricated from CO<sub>2</sub> through the intermediate, formaldehyde, and serve as an alternative to polyethylene and polypropylene. Although POM is more expensive than other polymers, it has better mechanical properties that can compensate for the higher price in certain applications [58, 59]. Furthermore, polyethercarbonate polyols (PECPs) are produced by the copolymerization of CO<sub>2</sub> and propylene oxide (PO), which were successfully used for preparing polyurethane (PU) foams by Langanke *et al.* [60] as demonstrated in **Fig. 4(a)**. As shown in **Fig. 4(b)**, PU foams prepared in this study show the same thermal stability when compared with the conventional PU materials. This implies that the large-scale polyethercarbonate polyols applications for PU production offer a new way to utilize carbon. One major concern for using CO<sub>2</sub>-derived polymers is the following decomposition of these polymers over several decades, releasing CO<sub>2</sub> back to the atmosphere [39].

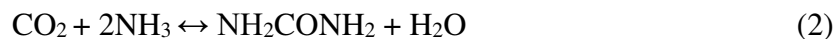




**Fig. 4** (a) Scanning electron micrograph of a flexible PU foam produced by toluene diisocyanate (TDI) and PECP (10.5 wt% CO<sub>2</sub>), (b) thermal stability of PECP and polyether (PE), and PU foams based on them; Reprinted with permission from Ref. [60].

### 2.1.3 Urea

According to the recent IPCC report [61], agriculture activities accounted for 23% of all anthropogenic GHGs emissions globally during 2007-2016. Fertilizers are widely used in the agricultural and forestry fields, and the synthetic nitrogen fertilizer accounts for around 70% of the global fertilizer use which is produced via reacting CO<sub>2</sub> with anhydrous ammonia during the synthesis [62]. Urea is a neutral fertilizer with the highest nitrogen content up to 46%, which is simple to store and does not present fire risks for the long-term storage. The most common method for producing urea is the steam reformation of natural gas which generates CO<sub>2</sub> and ammonia (see Eqs. (1-2)).



However, these urea fertilizers are normally derived from fossil fuels which also release net CO<sub>2</sub> emissions during the process of synthesis. At the same time, the feedstocks of fossil fuels are limited, and the gradual depletion inevitably reduces the supply security. The integrated systems of urea production and utilization using both fossil and renewable

energy have been proposed and reported. Gilbert et al. [63] came up with a novel process using H<sub>2</sub> rich syngas from biomass gasification instead of natural gas reforming during ammonia production, which reduced 65% of the GHG emissions compared with the conventional process. Koohestanian et al. [64] proposed a new design process of urea production from the power plants flue gas, and CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O from the tail gas were utilized in the process. The intensified approach decreased the environmental risks and produced the urea more than 1.68 t/t CO<sub>2</sub>. In addition, a concept of *Blue Urea* has been proposed which converted the captured CO<sub>2</sub> into valuable chemicals [62, 65]. In this process, the ammonium carbamate was produced via the reaction between CO<sub>2</sub> and NH<sub>3</sub> into the organic solvents, i.e. 1-propanol, ethanol or N, N-dimethylformamide (DMF). Then, it was utilized to produce urea in the presence of various catalysts. However, these integrated systems for urea production are still in the conceptual stage and operated under the controlled conditions. They need to be evaluated in the real conditions before the scaling up to commercial applications since the interactions among fertilizer, soil and crops are complex.

Although CO<sub>2</sub> can be widely converted to chemicals, liquid fuels and polymers, the CO<sub>2</sub> conversion processes consume a lot of energy. Renewable solar, wind, wave, hydropower, geothermal energy, and waste heat from plants should be the first consideration. For instance, the solar thermochemical technology is proved to be a novel and feasible pathway for CO<sub>2</sub> conversion using solar energy. The excessive solar electricity could be employed for the synthesis of renewable fuels during the summer which can be used during the winter. In terms of sustainable large-scale CO<sub>2</sub> utilization, the commodity products of these conversion processes should be economically viable and in high demand. Meanwhile, it is essential to evaluate the economic feasibility and energy balance of the conversion processes.

## 2.2 Mineralization

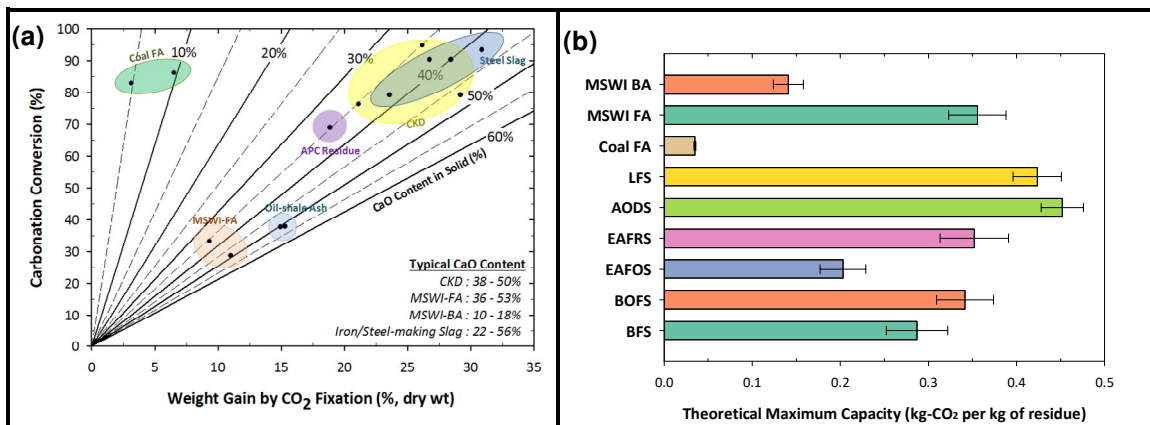
Industrial CO<sub>2</sub> emissions can be effectively utilized through mineralization processes (so-called accelerated carbonation) to form various products and/or carbonate precipitates, as it is a thermodynamically favorable reaction. A variety of feedstocks, such as natural silicate ores [66] and alkaline solid wastes [67, 68] can be utilized in CO<sub>2</sub> mineralization processes. Recently, mineralization using alkaline residues has become an attractive method for direct and indirect decrease in CO<sub>2</sub> emissions from industries and power plants [69, 70]. Despite the very large CO<sub>2</sub> capture capacity using natural ores, mineralization using alkaline solid wastes has other merits, such as low feedstock cost and availability near the source of CO<sub>2</sub>. Mineralization can be achieved through four main approaches [71]: (i) direct carbonation, *i.e.*, the reaction of CO<sub>2</sub> with alkaline slurry or mixture in a single reactor; (ii) indirect carbonation, *i.e.*, the extraction of ions of interest for the production of high-purity chemicals such as CaCO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> *via* multiple steps; (iii) carbonation curing, *i.e.*, the use of CO<sub>2</sub> for curing of cement-based materials to enhance their strength and durability; and (iv) electrochemical mineralization, *i.e.*, the use of an electrochemical cell to mineralize CO<sub>2</sub> while producing hydrogen or electricity. A number of large-scale CO<sub>2</sub> mineralization demonstrations have been carried out, and critically reviewed from technical and engineering-science perspectives [72].

Available alkaline solid residues include iron and steel slags [73, 74], incinerator ashes [75], fossil fuel residues [76, 77], cement and concrete waste [78, 79], mining and mineral processing waste [80, 81], and pulp/paper mill waste [82, 83]. They typically contain a large amount of alkaline earth metals (*i.e.*, calcium and magnesium), which can serve as suitable feedstocks for CO<sub>2</sub> mineralization. To examine the performance of different mineralization processes, Pan *et al.* [84] developed an integrated thermal analysis method and determined the relationship between carbonation conversion and weight gain for different types of solid residues. The integrated thermal analysis method accurately

quantifies the weight of reaction products after mineralization based on the interpretation of the thermogravimetric and derivative thermogravimetric (TG-DTG) plots. As shown in **Fig. 5(a)**, a relationship between carbonation conversion and weight gain of alkaline residues can be easily identified and compared. In general, a carbonation conversion above 85% for solid residues is acceptable to achieve waste stabilization and CO<sub>2</sub> fixation [85]. It should be noted that the carbonation conversion of alkaline residues represents the ratio of the actual amount to the theoretical maximum amount of CO<sub>2</sub> (denoted as ThCO<sub>2</sub>) that can be mineralized. According to the chemical compositions of solid residues, one can estimate the ThCO<sub>2</sub> (kg CO<sub>2</sub> per kg of solid residue on dry basis) by Steinour's equation [86]:

$$\text{ThCO}_2(\%) = 0.785 (\text{CaO} - 0.56 \text{CaCO}_3 - 0.7 \text{SO}_3) + 1.091 \text{MgO} + 1.420 \text{Na}_2\text{O} + 0.935 \text{K}_2\text{O} \quad (3)$$

where CaO, SO<sub>3</sub>, MgO, Na<sub>2</sub>O, and K<sub>2</sub>O are their weight fractions (per kg solid residue) obtained *via* X-ray fluorescence (XRF). CaCO<sub>3</sub> is the weight fraction analyzed by integrated thermal analysis.



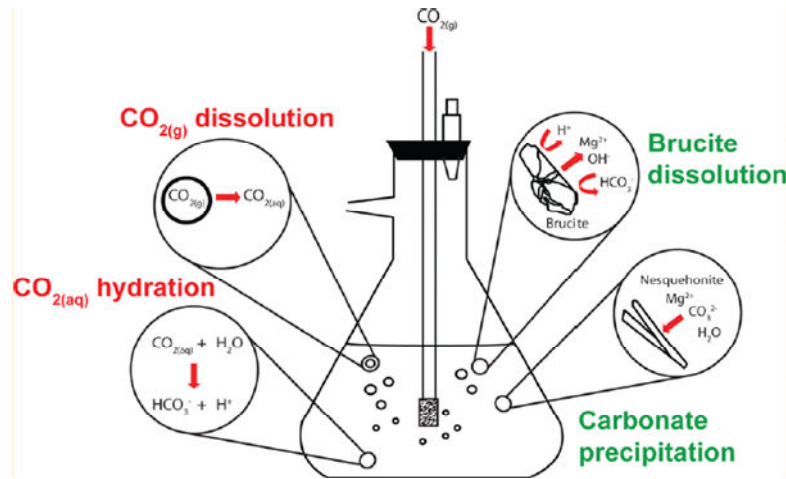
**Fig. 5 (a)** Relationship of carbonation conversion and weight gain for various solid residues. Acronyms: cement kiln dust (CKD), municipal solid waste incinerator (MSWI), fly ash (FA), and bottom ash (BA). Reprinted with permission from Ref. [84]. **(b)** Theoretical maximum capacity of CO<sub>2</sub> mineralization for different solid residues (with a 95% confidence interval). Reprinted with permission from Ref. [87]. Acronyms: ladle furnace

slag (LFS), argon oxygen decarburization slag (AODS), electric arc furnace reducing slag (EAFRS), electric arc furnace oxidizing slag (EAFOS), basic oxygen furnace slag (BOFS), and blast furnace slag (BFS).

**Fig. 5(b)** shows the values of  $\text{ThCO}_2$  for different solid residues based on integrated thermal analysis and Steinour's equation. In most cases,  $\text{ThCO}_2$  values for alkaline solid residues are proportional to the percent of calcium-bearing compounds. For instance, argon oxygen decarburization slags have a theoretical maximum capacity in the range of 0.43–0.48 kg  $\text{CO}_2/\text{kg}$ , determined based on their chemical compositions [87].  $\text{CO}_2$  also could be mineralized in several hours with magnesium-bearing compounds through the formation of  $\text{MgCO}_3$  under typical conditions of  $\text{CO}_2$  partial pressure  $>10$  MPa, and temperature  $>417.15$  K [88, 89]. Though the total amount of manmade alkaline solid residues is limited compared to natural ores/minerals, scale-up demonstrations should reduce some of the technical barriers to processing natural minerals for  $\text{CO}_2$  mineralization and utilization.

Compared to natural minerals, industrial solid residues are more reactive and usually available in a finely ground state, reducing or eliminating the need for additional pretreatment. The lack of reactivity of serpentine rock and similar minerals has been a major problem for mineralization of natural rocks and may demand grinding down to micron size and reaction in salt solutions at pressures up to 10 MPa or more, since in nature, reactions with  $\text{CO}_2$  are exceedingly slow [90, 91]. **Fig. 6** shows the mechanisms and important reaction routes of  $\text{CO}_2$  mineralization with brucite, in the case of using mine tailings. The mechanisms of  $\text{CO}_2$  mineralization using alkaline residue slurry can be described by three main steps: (i) dissolution of gaseous  $\text{CO}_2$  into the aqueous phase; (ii) dissolution of minerals; and (iii) precipitation of carbonates. To reduce the fresh water consumption as well as to enhance the mineralization performance, industrial wastewater [92] or concentrated brine [93] can be utilized for  $\text{CO}_2$  mineralization using alkaline solid

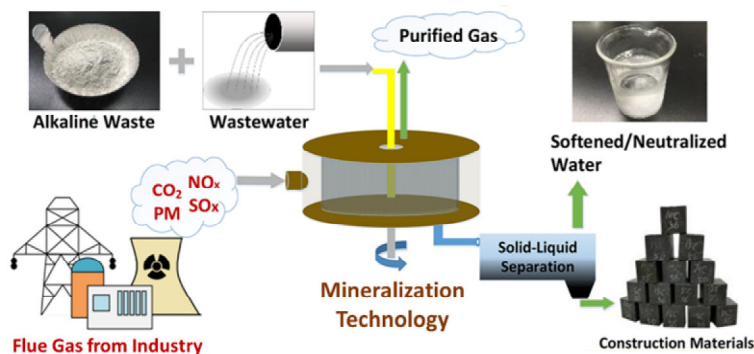
residues. In addition, the use of brine solution for CO<sub>2</sub> mineralization may enhance the dissolution of calcium- and magnesium-bearing silicate minerals [94]. Due to the chemical and mineralogical complexity of alkaline residues, further elucidation of reaction pathways and mechanisms at the interface of liquid-solid phases is needed to understand and improve the kinetics and mass transfer in the CO<sub>2</sub> mineralization processes.



**Fig. 6** Mechanisms and important reaction routes of CO<sub>2</sub> mineralization using alkaline residues, *e.g.*, brucite including Mg(OH)<sub>2</sub> in mine tailings. Reprinted with permission from Ref. [81].

CO<sub>2</sub> mineralization using alkaline solid residues can also be beneficial for air pollution control for various industries and/or coal-fired power plants (as depicted in **Fig. 7**). For instance, Pei *et al.* [71] evaluated the performance of high-gravity mineralization technologies using fly ash for the removal of air pollutants from the petrochemical industry. The results showed that the removal efficiencies for CO<sub>2</sub>, NO<sub>x</sub> and particulate matter were approximately 96%, 99% and 83%, respectively. The reacted solid residues can be used in construction as alternative cementitious materials in concrete or cement mortars [67]. The products from CO<sub>2</sub> mineralization should be engineered toward diverse applications in the built environment. For other mineralization approaches, the products from indirect carbonation also can be converted to high-value-added materials, such as geopolymers, abiotic catalysts, soil conditioners, glass ceramics and calcium carbonate precipitate.

Similarly, the electrochemical mineralization technologies can sequester gaseous CO<sub>2</sub> from various industries while generating electrical energy and NaHCO<sub>3</sub> product [95].



**Fig. 7** CO<sub>2</sub> mineralization using alkaline residues with integrated air pollution control from industries and power plants. Adapted from Ref. [71].

Although the amount of CO<sub>2</sub> that can be mineralized is limited in comparison to the total global CO<sub>2</sub> emissions, it offers the added benefits of remediating alkaline solid residues, as well as of generating marketable products from the solid residues. However, significant technological breakthroughs are required before deployment in a cost-effective manner can be realized. This includes novel reactor design, process intensification, heat integration and system optimization. The hybridization of CO<sub>2</sub> mineralization with other concepts or processes, such as integrated air pollution control or water reclamation, should be a future priority research direction. Also, several unit processes used in CO<sub>2</sub> mineralization, such as feedstock grinding, process heating and slurry stirring, consume a substantial amount of energy. Therefore, energy consumption of CO<sub>2</sub> mineralization needs to be compensated by recovering energy from the exothermic reactions to make the process economically viable in an industrial context [96-98]. To achieve a waste-to-resource supply chain, a system optimization from the energy, engineering, environmental, and economic sectors is also required [99].

### 2.3 Beverage and Food Processing

In the beverage and food industry, CO<sub>2</sub> can be utilized as an acidifying agent [100].

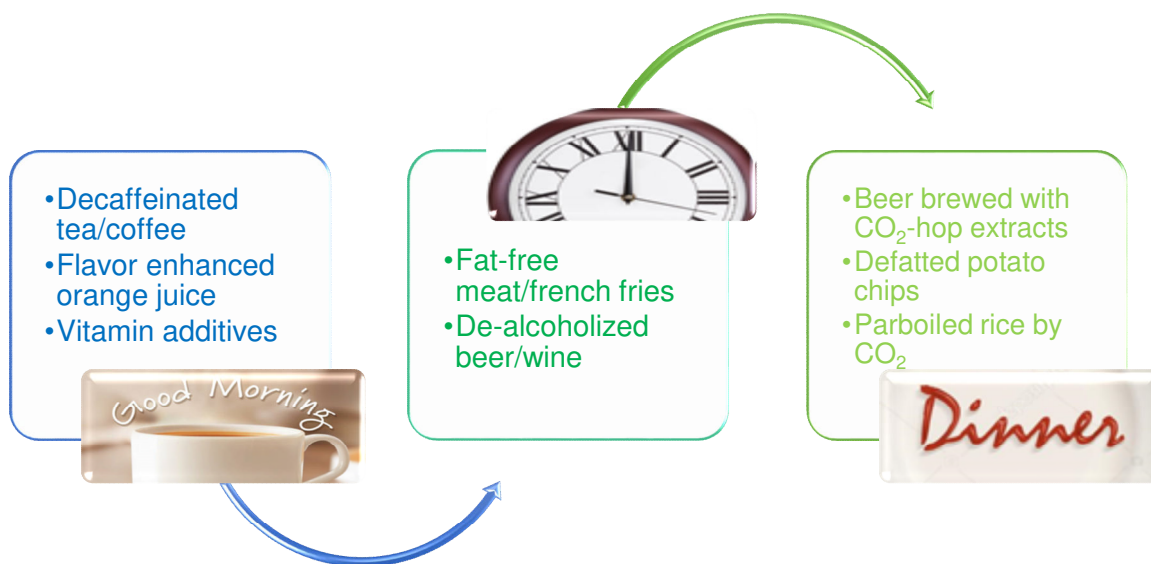


However, CO<sub>2</sub> purity is a very significant factor due to possible contamination of the final products from benzene, COS, and H<sub>2</sub>S from gasification processes and SO<sub>2</sub> and NO<sub>x</sub> from combustion sources. Currently, the main uses of food-grade carbon dioxide are in producing carbonated drinks, de-oxygenated water, milk products, and food preservation. Beer, soft drinks, and sparkling wine consume large quantities of liquid CO<sub>2</sub> for their production and, therefore, it is important that the CO<sub>2</sub> used comes from renewable sources or recycled CO<sub>2</sub>. In conventional food preservation, mechanical refrigeration is mainly used during transportation and storage. However, for foods that require freeze drying (dehydration), liquid carbon dioxide, dry ice (*i.e.*, the solid form of CO<sub>2</sub>) and modified atmosphere packaging (MAP) technologies are more widely used for refrigeration. The major limitation of such approaches is that “storage” is transitory, and the best justification of such technologies is if the source of CO<sub>2</sub> replaced represents “new potential off-set” CO<sub>2</sub> being released to the atmosphere, in which case careful life cycle analysis is needed to estimate the benefit of replacing CO<sub>2</sub> production from fossil fuels such as methane [101].

Supercritical fluid extraction (SFE) technology is an approach for utilizing CO<sub>2</sub> in the production of flavors and essential oils, and coffee decaffeination, which is beneficial to the separation and extraction of heat-sensitive, volatile and oxidizable components. In comparison with the traditional separation methods, it has the following advantages [102-104]: The extraction agent in SFE is typically non-toxic, non-corrosive, and chemically stable; SFE provides better permeability than other solvent techniques; The extraction capability of SFE can be controlled easily by adjusting the main operating parameters; and the extraction agent can be reused after decompression to save energy.

Thus, supercritical CO<sub>2</sub> extraction (SCE) technology is preferred in food manufacturing owing to the above merits. In 1978, SFE technology was first industrially employed in Germany for extracting caffeine from coffee beans [105]. Currently, this

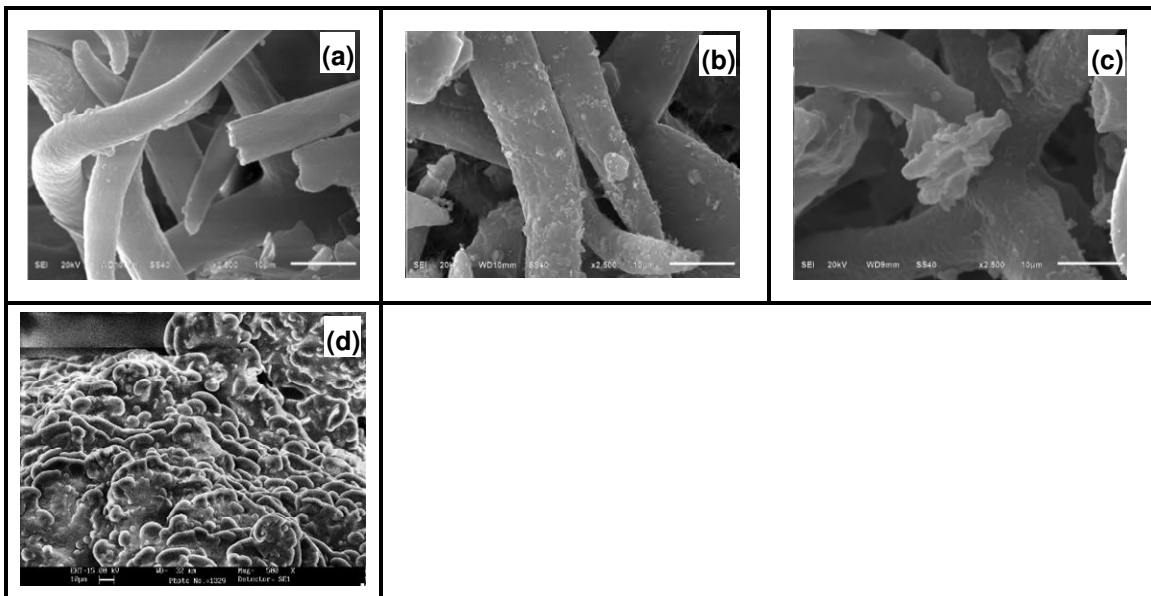
technology has been extensively applied in daily life as illustrated in **Fig. 8** [106]. Important applications of SFE technology include the extraction of oils and fat fractions [107-111], lipids and cholesterol [112, 113], natural colors [114], antioxidants [115, 116], and hops [117, 118], and decaffeination of tea and coffee [119-121].

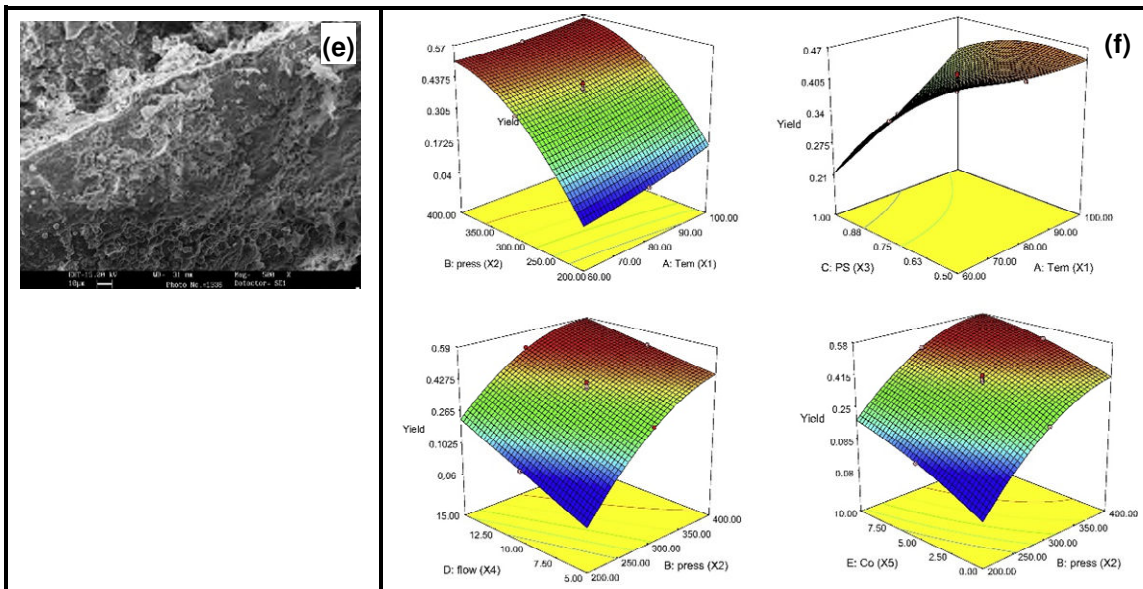


**Fig. 8** Representative daily food obtained by supercritical fluid extraction. Reprinted with permission from Ref. [106].

A number of essential oils (EOs) are widely used in foods or cosmetics. **Table S1** shows the extraction yields of EOs from various samples at the optimum operating conditions, *i.e.*, temperature, pressure, and extraction time reported in the recent literature. Importantly, SCE is found to exhibit better extraction performance than some other extraction technologies. Conde-Hernández *et al.* [122] claimed that CO<sub>2</sub>-supercritical extraction has higher antioxidant activity and oil yield, compared with steam distillation (SD) and hydrodistillation (HYDRO) methods. Micrographs of rosemary before and after SCE treatments are shown in **Fig. 9**, which provides a vivid description of the changes in the samples. The surface of the rosemary was smooth before treatment (**Fig.**

**9(a)**); however, the samples tended to collapse after exposure to the supercritical extraction under different temperatures and pressures (**Fig. 9(b)** and **9(c)**). Moreover, watermelon seed oil was extracted *via* SCE technology by Rai *et al.* [123]. As depicted in **Fig. 9(d)** and **9(e)**, the surface of the extracted seed layers was cracked and both oil and non-extracted phase were closely interpenetrating after the extraction compared to a rough surface before the extraction. The response surface methodology (RSM) was used to optimize the operating condition parameters including pressure, temperature, particle size, solvent flow rate, and co-solvent addition and obtain the maximum oil yields as shown in **Fig. 9(f)**. More recently, the SFE techniques assisted by other methods such as enzymes [124, 125], ultrasound [126, 127], and microwave [128-130], have been extensively reported. However, development of SCE technology must meet various hurdles due to the need for sophisticated equipment, difficulties in continuous production, and relatively high costs of the pilot-scale equipment, which slow the development of this technology.





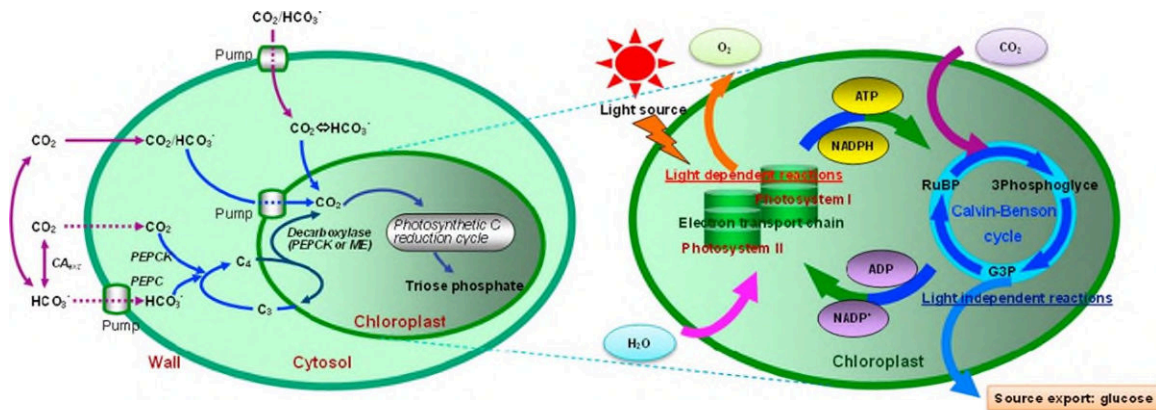
**Fig. 9** Scanning electron microscopy (SEM) images of rosemary (a) before SCE treatment, and after SCE treatment (b) at 10.34 MPa and 323 K, and (c) at 17.24 MPa and 313 K. Watermelon seed (d) before SCE treatment, and (e) after SCE treatment, (f) maximum oil yields with different condition combinations. Reprinted with permission from Refs. [122, 123].

## 2.4 Biological Utilization

In nature,  $\text{CO}_2$  is converted to carbohydrates through photosynthesis, as part of the natural carbon cycle. The biological fixation of  $\text{CO}_2$  is a safe and cost-effective method using plants and autotrophic microorganisms. In particular, autotrophic microorganisms are advantageous because of their small volume, high photosynthetic rate, strong environmental adaptability, rapid reproduction, high processing efficiency, and easy integration with other technologies. It has been noted that 1 kg algal biomass can fix about 1.83 kg  $\text{CO}_2$  [131]. Thus, research on microalgae has attracted great attention globally, especially as it could be used as an alternate energy source displacing fossil fuels [132, 133].

The carbon sources obtained for microalgae are mainly from the inorganic carbon dissolved in water. During the photosynthesis process of microalgae,  $\text{CO}_2$  is first fixed by

ribulose biphosphate carboxylase-oxygenase (Rubisco), and then converted to organic compounds using light energy through the Calvin-Benson cycle (C<sub>3</sub> cycle). Since the Rubisco carboxylase reaction is inhibited by high O<sub>2</sub> concentrations, the photosynthetic organisms have developed special mechanisms to adapt to variations in the gas composition. In particular, the carbon concentrating mechanism (CCM) is a typical process as shown in **Fig. 10** [134]. In a recent study, up-to-date developments in worldwide CCM research and the molecular components' effect on CCM enhancing carbon biofixation were discussed by Singh *et al.* [135]. The CCM system needs to be further studied to identify the most effective algae species.



**Fig. 10** Schematic of carbon concentrating mechanism process. Reprinted with permission from Ref. [134].

The selection of microalgae type is closely related to the desired application. For CO<sub>2</sub> from flue gas, the microalgae not only need a highly-efficient CO<sub>2</sub> fixation ability, but also the ability to survive high temperature, high CO<sub>2</sub> concentration (10-20%), and the presence of other gases such as NO<sub>x</sub> and SO<sub>x</sub>. For trace CO<sub>2</sub> (below 0.1%) in an enclosed reaction apparatus, it should have a wide range of pH, and high CO<sub>2</sub> conversion rate [136, 137].

**Table 1** lists the common use of different microalgae for CO<sub>2</sub> fixation.

**Table 1** CO<sub>2</sub> fixation performance using different algae.

<b>Algae</b>	<b>Temperature, K</b>	<b>CO<sub>2</sub> level, vol%</b>	<b>Maximum CO<sub>2</sub> fixation rate, g/(L·d)</b>	<b>Ref.</b>
<i>Anabaena sp.</i>	308	10	1.010	[138]
<i>Botryococcus braunii</i>	298	5	0.497	[139]
<i>Botryococcus sp.</i>	303	10	0.257	[140]
<i>Chlorella pyrenoidosa</i>	298	10	0.260	[141]
<i>Chlorella sorokiniana</i>	298	4.1	0.251	[142]
<i>Chlorella sp.</i>	303	10	0.252	[140]
	293	5	0.700	[143]
	298	5	0.252	[139]
	298	0.093	3.552	[144]
<i>Chlorella vulgaris</i>	303	1	6.240	[145]
	298	5	0.162	[146]
	298	2	0.430	[147]
<i>Dunaliella tertiolecta</i>	298	5	0.272	[139]
<i>Euglena gracilis</i>	300	10	0.074	[148]
<i>Nannochloropsis sp.</i>	303	10	0.265	[140]
	303	12	0.140	[149]
<i>Scenedesmus</i>	301	10	0.549	[150]
<i>obliquus</i>	301	20	0.390	[151]
	298	10	0.288	[141]

<i>Scenedesmus sp.</i>	298	2.5	0.368	[152]
	303	10	0.210	[140]
<i>Spirulina platensis</i>	298	5	0.319	[139]
<i>Spirulina sp.</i>	303	6	0.220	[149]

Physiochemical parameters during the fixation process, such as culture temperature, CO<sub>2</sub> concentration, light, and pH value, have an impact on the biofixation of CO<sub>2</sub> [153]:

(1) Culture temperature is an important factor for the photosynthesis efficiency of microalgal-carbon biofixation. Generally, microalgae also have an optimum growth temperature range of 291 to 298 K. Extremely high or low temperatures slow down the microalgal growth, by reducing the activity of Rubisco, which is the key plant enzyme for CO<sub>2</sub> fixation [101].

(2) In the past decades, the photobioreactor (PBR) or enclosed cultivation system was widely used. Light (sunlight or artificial light) plays a significant role in microalgae growth, reactor design and system operation, providing the energy for assimilation and activating some enzymes involved in the photosynthesis. However, long-time exposure can easily cause aging of the equipment, and the operation of the equipment may be affected by heat generation from the illumination [134].

(3) The pH can easily reach a high value of 10 under the conditions of high-density cultivation and without the supplement of CO<sub>2</sub>. In addition, a high-pH environment seriously affects the photosynthetic reaction process and cell uptake of nutrient salts, which leads to a decrease of microalgae biomass yield. Therefore, during the cultivation of the algae, the pH should be stabilized and managed to be neutral (pH = 6–8) [154].

(4) CO<sub>2</sub> concentration has an impact on the growth of the microalgae, and in general, a suitable value is 10-20% [155]. It is possible to use fossil fuel flue gas or the gas emissions from the steel and cement industries directly. Also, some types of microalgae show good

growth performance at higher CO<sub>2</sub> concentrations. For example, *Chlorococcum littorale* has a better growth performance when CO<sub>2</sub> concentration is higher than 40% [156, 157]. *Synechocystis aquatilis* has also been proved to grow with a CO<sub>2</sub> concentration of 40% [158]. These studies could help to improve microalgae tolerance using high concentrations of CO<sub>2</sub> from fossil fuel combustion flue gas. More research is also being devoted to genetically modifying algae to improve their ability to capture CO<sub>2</sub> [159].

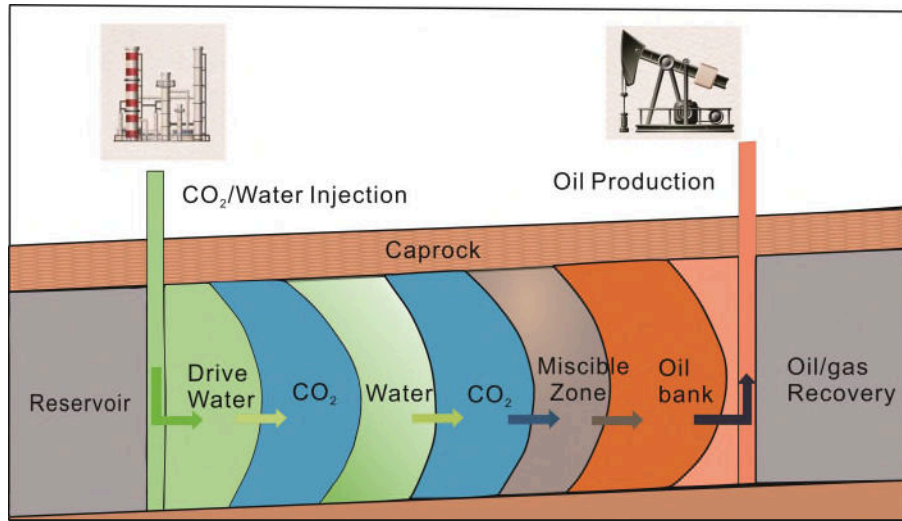
## 2.5 Enhanced Oil Recovery, Coal Bed Methane and CO<sub>2</sub> Fracking

Geologic CO<sub>2</sub> storage involves injecting captured CO<sub>2</sub> into underground reservoirs with suitable geological conditions, where CO<sub>2</sub> can be securely stored underground for more than 10,000 years [160]. However, it is possible to inject CO<sub>2</sub> into oil and gas reservoirs to enhance the production of fossil fuels [161]. CO<sub>2</sub> could be injected into depleted oil reservoirs, shale formations and unmineable coal seams for tertiary recovery or enhanced oil recovery (EOR), enhanced shale gas recovery (ESGR) and enhanced coalbed methane (ECBM) recovery, respectively. A future possible use of CO<sub>2</sub> is utilization as a fracturing fluid, thus eliminating or reducing the use of water [162].

The EOR method refers to extracting crude oil from oilfields, which could not be extracted by primary and secondary recovery. Three main techniques for EOR are chemical injection (*e.g.*, polymer flooding and surfactant-polymer injection), thermal injection (*e.g.*, *in situ* combustion, steam flood, and steam stimulation), and gas injection (*e.g.*, natural gas, CO<sub>2</sub>, and N<sub>2</sub>) [163-165]. Among these, since the 1970s CO<sub>2</sub> has been most commonly utilized for miscible displacement (**Fig. 11**), due to decreasing oil viscosity and a cheaper cost than liquefied petroleum gas (LPG). Stewart *et al.* claimed that there can be net emissions of CO<sub>2</sub> when the maximum utilization of CO<sub>2</sub> (CO<sub>2</sub> EOR+) process could store more carbon than produced [166]. CO<sub>2</sub>-EOR projects in operation are mainly in the US and Canada, which are also associated with available sources of CO<sub>2</sub>. The number of projects is growing in other regions such as China and Australia since CO<sub>2</sub>-EOR is treated

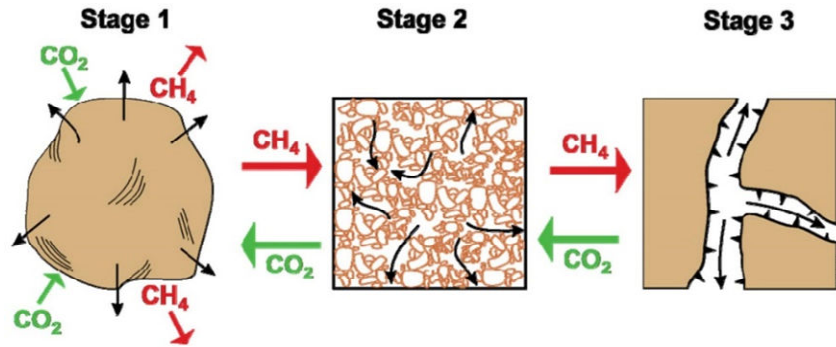


as an early CCUS adoption [167, 168]. Higher than 90% of the oil reservoirs worldwide might be suitable for using CO<sub>2</sub>-EOR technology [169]. Four important factors should be considered for further expanding CO<sub>2</sub>-EOR technology including the monitoring of underground and vented emissions, strengthening the risk management to the site capacity, and improving the utilization of the abandoned fields.



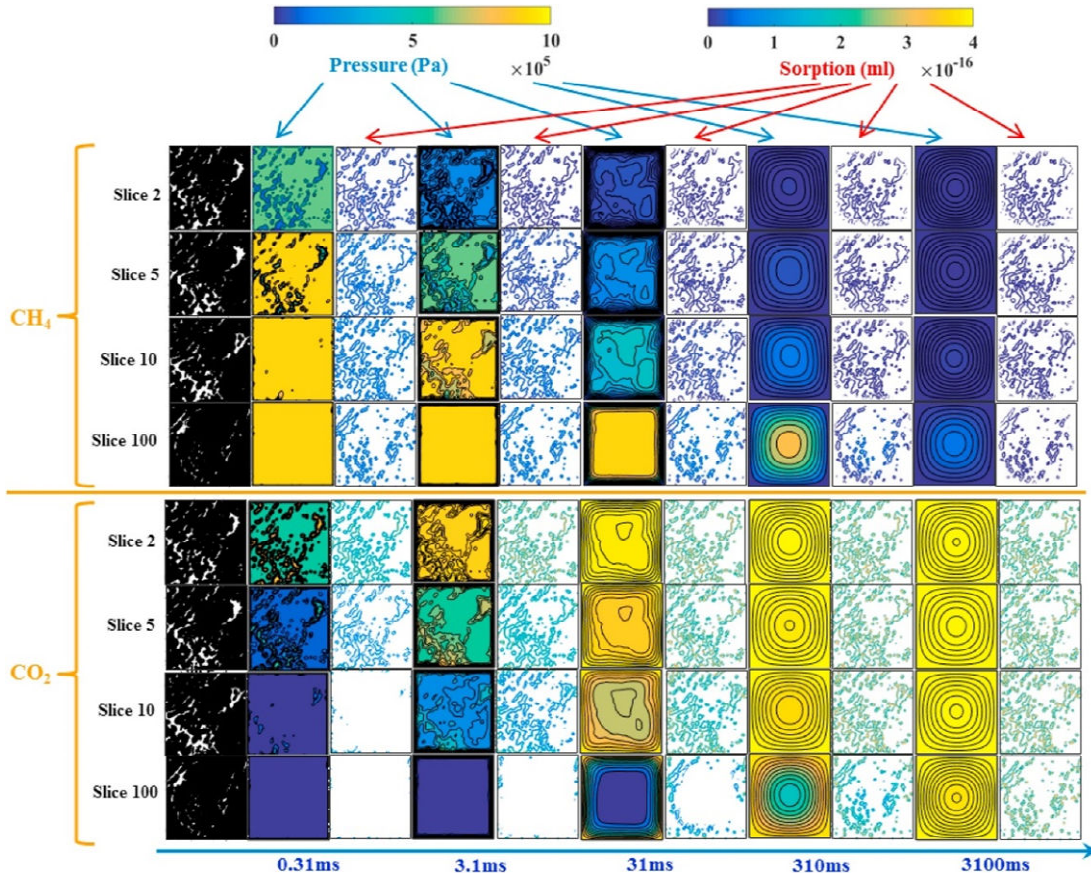
**Fig. 11** Schematic of CO<sub>2</sub>-EOR process.

Shale gas has become an important alternative to natural gas (*i.e.*, unconventional natural gas) over the past decade. CO<sub>2</sub> injection to enhance shale gas recovery in gas reservoirs is also an effective technique to improve the gas yield [170, 171]. CO<sub>2</sub> is also potentially more soluble than CH<sub>4</sub> in geological formations, and can replace desorbed CH<sub>4</sub> in pores and fractures, thereby increasing the recovery rate as depicted in **Fig. 12** [172]. To date, a large number of experimental and theoretical studies have been carried out on ESGR considering different influence factors such as reservoir and gas injection pressures [173-175], injection and production time [176-178], and physical characteristics of the reservoir [179, 180]. This method is also proven to be a feasible means of natural gas recovery [181]. Injecting CO<sub>2</sub> into gas hydrates to extract natural gas has attracted increasing interest [67, 182]. As a result, future research will likely be carried out to help commercialize this technology, in order to provide a route to long-term storage of CO<sub>2</sub>.



**Fig. 12** CH<sub>4</sub> and CO<sub>2</sub> flow dynamics in gas shales. Reprinted with permission from Ref. [172].

Moreover, CO<sub>2</sub> can be injected into deep coal seams (*i.e.*, ECBM), which not only improves coalbed methane recovery, but also sequesters CO<sub>2</sub>. The mechanisms of CO<sub>2</sub>-ECBM are presented in **Fig. 13**. A number of modeling, lab-scale studies, and small-scale field CO<sub>2</sub>-ECBM tests have been conducted. For example, Sun *et al.* [183] simulated the distributions of gas pressure and gas sorption performance during CO<sub>2</sub>-ECBM (**Fig. 13**). They noted that gases were mainly absorbed in the pores, and CH<sub>4</sub> diffused from the interior to the exterior of the samples, while CO<sub>2</sub> diffused in the opposite direction. However, almost all CBM is currently produced by removing water from the coal seam that decreases the pressure and enables CH<sub>4</sub> release from the coal. A detailed understanding of CO<sub>2</sub> sorption in reservoir conditions is needed to accelerate the commercial deployment of the technology.



**Fig. 13** Gas sorption and its pressure distributions in coal *via* CO<sub>2</sub>-ECBM technology (at 1 MPa). Reprinted with permission from Ref. [183].

## 2.6 Leading and Promising Utilization Technologies

The recovered CO<sub>2</sub> has already been stored in oil and gas wells and aquifers, and underground cavities also provide more possibilities. The CO<sub>2</sub> injection method for EOR has been employed in several regions. However, there are potential issues such as water supply leakage or acidification, which are still not completely understood, and transportation of supercritical CO<sub>2</sub> is also energy-intensive. In order to promote this technology, corrosion and other CO<sub>2</sub> transportation pipeline problems should be solved [184].

Ultimately, CO<sub>2</sub> conversion methods require different energy inputs, and renewable energy sources such as wind or solar power, which themselves have a minimal carbon

footprint, are the most obvious energy sources for such processes, where the energy for such processes is not used directly to make electricity, *i.e.*, stranded energy resources. If the prices of renewable energy continue to decrease, it could enable greater utilization of the energy for CO<sub>2</sub> conversion via chemical or catalytic approaches. Thus, microalgae can be a solution to produce liquid fuels and achieve CO<sub>2</sub> emission reduction. However, to make such methods economically viable, governments will need to intervene in the market. One major advantage of microalgae is the fact that such developments, especially no land use competition, are likely to receive significant public support [185]. Key challenges for such technologies include increasing the lipid content and also its conversion to biofuels with low CO<sub>2</sub> emission and energy consumption. It is important also to realize that such technologies will have specific geographic locations for early production or adoption based on local conditions and resources. In the short term, the production of simple industrial chemicals such as urea, methanol, and methane are still the most mature and closer to commercial application and are demanded in large volumes, making them more interesting if the goal is to reduce anthropogenic CO<sub>2</sub> emissions. Interestingly, integrated systems using different utilization methods may be a promising solution such as methanol production integrated with enhanced gas recovery (EGR) [186], or methanol and dimethyl ether synthesis [187].

CO<sub>2</sub> can be used in a number of ways, leading to different disposal options and making their evaluation difficult to quantify. Before the commercialization of these CO<sub>2</sub> utilization methods, the life cycle assessment (LCA) or techno-economic analysis (TEA) is beneficial to help identify promising utilization pathways [58, 188]. According to the tutorial review by von der Assen *et al.* [188], LCA is able to identify environmentally promising routes for CDU even in the early development stage. A variety of comprehensive reviews have focused on studying the life cycle environmental effects of different CDU strategies or a specific CO<sub>2</sub> utilization approach in detail [189-191], which can provide future insights for suitable CO<sub>2</sub> utilization pathways in particular instances. Therefore, the ideal methods

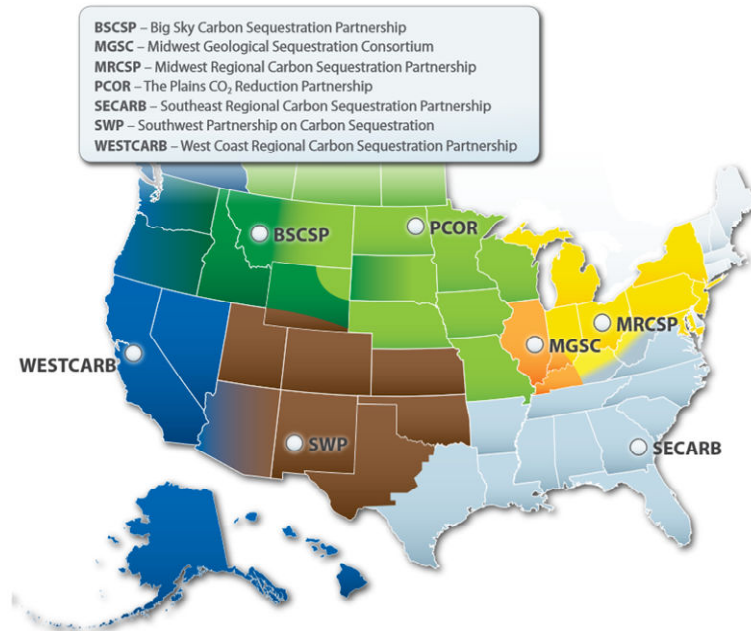
for CO<sub>2</sub> utilization need low additional energy, simpler reaction mechanisms and high future market size and value.

### 3 Trends in Global CO<sub>2</sub> Utilization Projects

In this decade, a variety of facilities to utilize CO<sub>2</sub> throughout the world have been operated, constructed, or announced, involving different-scale applications. These ongoing R&D projects are at the various stages of technological readiness but all are located in or are led by technologically advanced countries.

#### 3.1 United States

The United States leads the deployment technology of CCS in the world especially the EOR technology. The United States Department of Energy (DOE) has promoted the CCS knowledge base *via* a wide portfolio of research projects since 1997. Three technologies in the United States for CO<sub>2</sub> utilization are focused on boosting the commodity market for CO<sub>2</sub>, including chemicals, mineralization, and polycarbonate plastics. These methods are expected to be in large-scale testing by 2030, with widespread commercial applications by 2035. To support the development in the regional infrastructure for CCS, seven Regional Carbon Sequestration Partnership (RCSP) regions have been created since 2003, as shown in **Fig. 14** [192]. Approximately \$2.66 billion has been invested by DOE in 794 different-scale R&D projects since 2010 [193]. Meanwhile, the United States has increased the carbon tax credit to \$35/t for EOR use and \$50/t for storage in saline formations by 2026, which was initially \$10/t in 2008 [194]. In addition, the United States is collaborating with various global organizations on CDU and CCS projects.



**Fig. 14** United States Regional Carbon Sequestration Partnership network [192].

### 3.2 China

In China, R&D activities on CCS are mainly financially supported by the government and conducted by industrial companies with the joint participation of universities or research institutes. One of the national key scientific and technological projects of “Large Oil and Gas Fields and Coal Seam Gas Development Projects” invested more than \$40 million to promote demonstration of the CO<sub>2</sub>-ECBM and CO<sub>2</sub>-EOR techniques [195]. In 2018, the first large-scale CCS facility was commenced by China National Petroleum Company [196]. Furthermore, the Chinese government actively participates in the Carbon Sequestration Leadership Forum (CSLF), Clean Energy Ministerial (CEM) conference and some international frameworks, and supports domestic research institutes and companies involved in bilateral and multilateral cooperation projects [195]. Currently China owns the largest number of CCS pilot and demonstration plants in operation, construction, and planning.

### 3.3 United Kingdom

Since 2017, the United Kingdom government has announced new strategies (*e.g.*, Clean Growth Strategy) to support advancements in carbon capture, usage and storage. Three routes are promoted: development of innovative technology, development of international collaboration on CCUS, and research on reducing costs in CCUS projects. A number of CCUS deployment projects are planned to start in the next two or three decades. The government has invested more than £130 million on CCUS R&D and innovation since 2011. In addition, £20 million has been allocated to design and support CCU demonstration projects for developing innovative techniques [197]. More recently, the government awarded £26 million to advance CCS, and the largest CO<sub>2</sub> capture project to date in the United Kingdom will be able to remove and use 40000 t/y CO<sub>2</sub> [198]. Even allowing for the United Kingdom leaving the EU, there will be little effect on the current Energy policy due to its Climate Change Act [198]. This requires that the United Kingdom reduce CO<sub>2</sub> emissions by 80% from 1990 levels by 2050 to meet its CO<sub>2</sub> emissions target.

### 3.4 Australia

The Australian government is involved in a variety of international forums that aim to promote the development and deployment of CCS such as CSLF, the Australia-China Joint Coordination Group and others within and beyond the Asia Pacific region. The China Australia Geological Storage (CAGS) projects included: Phase 1 on clean development and climate (from 2009 to mid-2012); Phase 2 on clean coal technology (from mid-2012 to 2015); and Phase 3 on bilateral CCS/CCUS cooperation (from 2016 to 2018) [199].

### 3.5 Norway

Norway has deployed two commercial-scale CCS projects at Sleipner in 1996 and at Snøhvit in 2007 [200]. In 2018, the Norwegian government allocated about €29 million to promote CCS deployment including the funding for two full-chain CCS projects. Each

project will capture 400 billion t per annum of CO<sub>2</sub> for storage below the North Sea seabed. More recently, the government announced funding of about €36 million to the CCS exploration well in April 2019 [201].

### 3.6 Germany

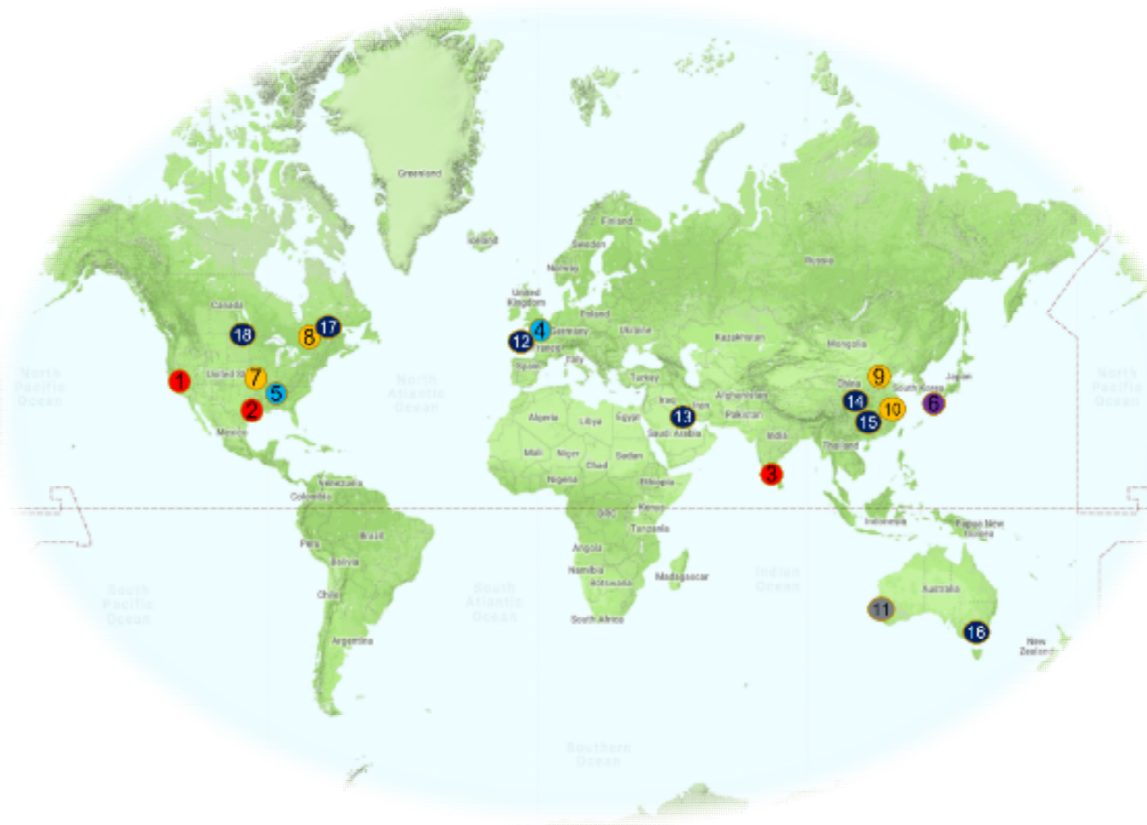
Since 2002, the German government has set goals for combatting climate change, *i.e.*, decreasing GHG emissions by 40% (2020) and 80% (2050) compared with 1990 levels [202]. In 2015, they renewed the targets as “New High-Tech-Strategy” that defines the major future directions. From 2010 to 2016, 33 CDU projects were granted, through the government, around €100 million in total, and €50 million was paid by various industries to support research projects [203]. Furthermore, the German Federal Ministry of Education and Research (BMBF) employed the efficient integrated method considering the scientific and socio-economic competencies in climate services. In order to trigger innovations, Germany supports a wide range of R&D programs for CDU.

### 3.7 Future Directions in R&D Projects

Currently, a number of projects for CO<sub>2</sub>-EOR, CO<sub>2</sub>-ECBM, and CO<sub>2</sub> storage in saline aquifers are ongoing worldwide [204]. **Fig. 15** shows the facilities with a scale of 400 t/d or more of CO<sub>2</sub> utilization (non-EOR). Approximately 20 CDU projects are being operated or under construction. CO<sub>2</sub> could be used in several industrial fields such as mineralization, food and beverage, and algae cultivation, which could promote scaled-up applications of CCS technology [205]. Most of the R&D projects are centered on the power generation industry, especially coal power generation. However, the great majority of the R&D projects are still in the early stages, and have not yet reached the pilot-plant scale. Both Petra Nova (United States) and Boundary Dam (Canada), two commercial large-scale electricity-generating plants with CCS, could offset the CCS cost via selling CO<sub>2</sub> for EOR [206]. In Europe, the Norwegian CCS projects are successful due to the high national



carbon taxation and two offshore storage projects, *i.e.*, Port of Rotterdam CCUS project and Norway full-chain CCS, will be expanded in future [207]. It indicates that increasing the carbon tax credits could incentivize more investments in large-scale CCS deployment and boost the confidence in the private sector. In the future, R&D projects should be concentrated on finding pathways to process intensification of CO<sub>2</sub> utilization, taking capture cost and policy support into account. Unfortunately, the development of such R&D projects is challenging due to their complexity and financial barriers [208].



- Mineral Carbonation**
1. 🇺🇸 Searles Valley Minerals CO<sub>2</sub> Capture Plant
  2. 🇺🇸 Skyonic Carbon Capture and Mineralization Project
  3. 🇮🇩 Tuticorin CDU Project
- To Be Confirm**
4. 🇫🇷 Port Jérôme CO<sub>2</sub> Capture Plant
  5. 🇺🇸 Supercritical CO<sub>2</sub> Pilot Plant Test Facility
- Algae Cultivation**
6. 🇯🇵 Saga City Waste Incineration Plant
- Food and Beverage**
7. 🇺🇸 AES Shady Point & Warrior Run CO<sub>2</sub> Recovery Plants
  8. 🇨🇦 Saint-Felicien Pulp Mill and Greenhouse Carbon Capture Project
  9. 🇨🇳 Huaneng Gaobeidian Power Plant Carbon Capture Pilot Project
  10. 🇨🇳 Shanghai Shidongkou 2<sup>nd</sup> Power Plant Carbon Capture Demonstration Project
- Residue Carbonation**
11. 🇦🇺 Alcoa Kwinana Carbonation Plant
- Various Utilization**
12. CO<sub>2</sub> Utilization Plants – Europe
  13. 🇩🇪 SABIC Carbon Capture and Utilization Project
  14. 🇨🇳 Chongqing Hechuan Shuanghuai Power Plant Carbon Capture Industrial Demonstration Project
  15. 🇨🇳 CO<sub>2</sub> Recovery Plants
  16. CO<sub>2</sub> Utilization Plants – Oceania Region
  17. 🇨🇦 The Valorisation Carbone Québec (VCQ) Project
  18. CO<sub>2</sub> Utilization Plants – North America
  19. CO<sub>2</sub> Utilization Plants by the Fluor Econamine FG Process (multiple locations)
  20. CO<sub>2</sub> Utilization Plants by the KM CDR Process® (multiple locations)

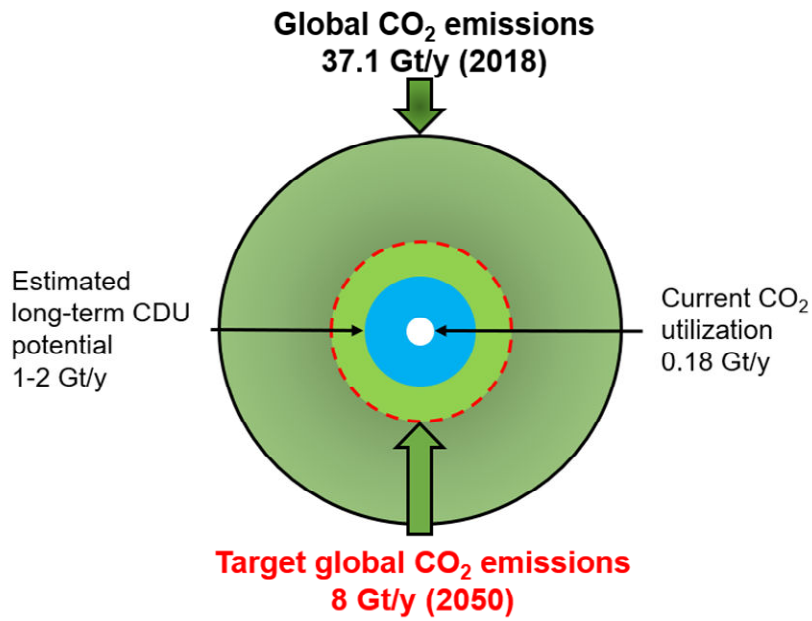
**Fig. 15** Distribution of large-scale CO<sub>2</sub> utilization projects around the world.

## 4 What is the Potential CO<sub>2</sub> Market?

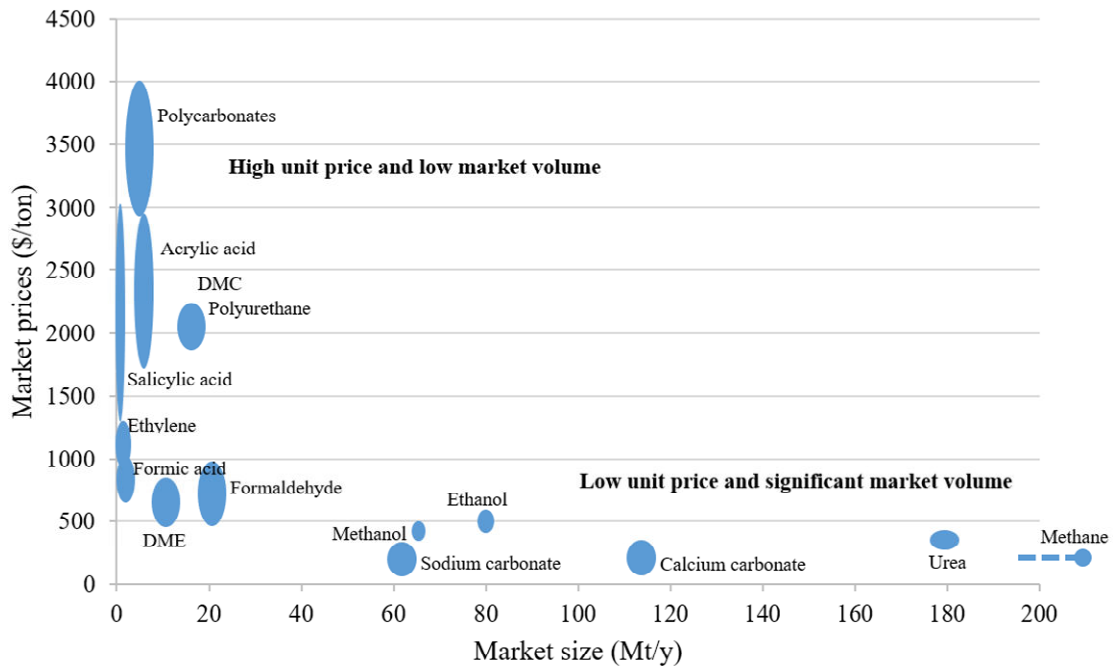
### 4.1 Market Scale and Value

The size of the individual CO<sub>2</sub> utilization markets varies from country to country, which could affect the climate benefit from the CDU approaches. The demand for products using CO<sub>2</sub> is increasing gradually. As illustrated in a recent report [209], the CO<sub>2</sub> market throughout the world will exhibit an annual growth rate of more than 13% by 2022. **Fig. 16** displays the potential CO<sub>2</sub> utilization in 2050 compared to global CO<sub>2</sub> emissions, indicating the enormous markets for CO<sub>2</sub> use [210, 211]. However, the CO<sub>2</sub> utilization potential is relatively small compared to the 37.1 Gt/a global CO<sub>2</sub> emissions (2018), but could offer the potential of using up to, say, 10% of anthropogenic CO<sub>2</sub> for the production of products like methanol [212]. Use of CO<sub>2</sub> is not a substitute for storage due to the large amounts of CO<sub>2</sub> needed to be stored. Oil and gas industries are the main contributors to the CO<sub>2</sub> market for EOR. For instance, the billions of tonnes of CDU potential in the cement and aggregates industries represent low-margin, highly standardized markets that are difficult to penetrate with new products. As shown in **Fig. 17**, significant unit price and high market volume of products cannot be obtained simultaneously. It is recommended that the focus should be on four categories of CO<sub>2</sub> utilization markets: building materials (such as carbonate aggregates and concrete); chemical intermediates (such as formic acid, methanol, and syngas); fuels (such as methane and liquid fuels); and polymers. For instance, the current market size of methane is 3-4 trillion cubic meters per year (Mt/y), estimated to be 4-5 trillion cubic meters annually by 2030. Urea exhibits a market size of 180 Mt/y with a cheap unit price. The main barriers are low-cost catalysts and the integrated processes of carbon capture and conversion and renewable energy [213]. However, the high cost of these technologies still hampers the growth of the market. Some of the technologies are still at an early development stage, thus the cost/performance should be considered. The methods for utilizing CO<sub>2</sub> need further scale-up by improving the market size and

manufacturing capacity in pilot to commercial plants.



**Fig. 16** Comparison between CO<sub>2</sub> emissions and utilization potentials.



**Fig. 17** CO<sub>2</sub> utilization market potential and value comparisons. Reprinted with permission from Ref. [214].

## 4.2 Regulation and Policy

The possibility of failure still exists in the present CCS market. Thus, without a well-designed policy, the private sector will not invest in CCS at the scale necessary to achieve climate change mitigation targets. A stable regulatory framework is needed to help companies reduce and avoid the negative impacts of failure and increase the financial return from the investment. Therefore, well-designed policies for CO<sub>2</sub> utilization are very important to start and build markets. Currently, the range of government policies supporting the deployment of CCS is wide, including carbon pricing, taxes, reporting requirements, government procurement, market mandates (*e.g.*, a low- or zero-emissions portfolio standard) and shareholder actions. In many cases, the products need to meet current standards to be accepted in the marketplace. These standards are normally supervised by the government and industry members, and developed by consensus-based and voluntary committees. Currently, there are few incentives to update or revise the present criteria. Even where the willingness exists, changes to regulatory frameworks are slow and are certainly lagging demand for CO<sub>2</sub> reduction [5].

Currently, planning and investment decisions are hampered by a lack of information, the dynamic nature of the technology and the markets, and the changing policy landscape. In general, individual attitudes to accept CO<sub>2</sub> utilization technologies and products are positive due to the perceived goal of reduction in CO<sub>2</sub> emissions. It is important that the public receives adequate information provided by governments to increase their interest and confidence. Governments should engage early with standards-setting organizations to avoid delays in market entry of these products and expand an innovative agenda for CO<sub>2</sub> utilization. Currently, there are only a few countries with specific policy measures to support the deployment of CCS including Norway, the UK, the US, China, Canada, and Japan [215]. In the long term, the government policies are central to increasing the deployment of these technologies and without these drivers CO<sub>2</sub> use cannot make a

significant contribution to meet climate goals. The procurement for CO<sub>2</sub> products and climate policies must be aligned as we are serious about meeting the targets. That being said, utilization might, for instance, compensate for hard-to-control areas such as aviation, and is in any case a logical direction for a carbon-constrained world.

## **5 Conclusions and Recommendations**

Increasing atmospheric CO<sub>2</sub> concentration is regarded as a major contributor to climate change. Although CO<sub>2</sub> capture technologies are relatively mature, the utilization of captured CO<sub>2</sub> remains an important challenge which needs much future research. The development of novel LCA and techno-economic tools and benchmark assessments will enable consistent and transparent evaluation of CO<sub>2</sub> utilization pathways in the short to medium term. Currently, there exist some limitations to further developing CDU such as energy and water consumption, the use of expensive catalysts, and gas infrastructure issues. In particular, cost-effective CO<sub>2</sub> utilization methods are required, and their pilot-scale demonstrations are critical for their commercial deployment. It is evident that the comprehensive introduction of different CO<sub>2</sub> utilization methods is beneficial to understanding the mechanisms and choosing appropriate techniques for use of captured CO<sub>2</sub>. The potential integrated technologies are preferable to make up the present gaps for broad industrial applications. Furthermore, the demonstration of R&D projects for CDU and analysis of CO<sub>2</sub> utilization markets are advantageous to identify the possibility of full-scale deployment of these technologies.

To promote development of the industrial feasibility of CDU technology, economic viability is critical whether this is achieved by means of technical development or policy changes. Thus, future primary research interests should be focused on the areas of CDU and CCS regulations, policy and assessments, and integration of CO<sub>2</sub> utilization with other techniques to reduce energy consumption and costs, especially at a larger scale. Meanwhile, in order to improve public awareness of the environmental impacts, public education and

publicity on CCUS should be emphasized, and international collaborations need to be further enhanced. It should also be emphasized that CDU is not an alternative to CCS, but rather an adjunct and that without CCS we will fail to meet our climate goals. Governments should increase their commitment to CCUS and play a crucial role in promoting its deployment (*e.g.*, tax incentives, financial options, and policies) to maintain the global mean temperature increase below 1.5 °C. Another effective strategy is to encourage private sector investments for larger-scale demonstration programs and commercialization of CDU technologies. In the near future, CO<sub>2</sub> may become a resource which will be demanded by different sectors of the global economy and affect the regulation and policy to the CO<sub>2</sub>-based products market.

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