

# MEETING THE DUAL CHALLENGE

A Roadmap to At-Scale Deployment of  
CARBON CAPTURE, USE, AND STORAGE

## CHAPTER NINE – CO<sub>2</sub> USE



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# Chapter Nine

## CO<sub>2</sub> USE

### I. CHAPTER SUMMARY

**C**arbon dioxide use converts CO<sub>2</sub> into valuable products through chemical reactions or biological conversions. The CO<sub>2</sub> used can be sourced from natural or anthropogenic sources. Carbon is used to produce fuels, polymers, industrial chemicals, carbon nanotubes, and building products such as carbonates and cement. It is also used in the production of steel, electronics, and consumable goods. Some CO<sub>2</sub>-derived products, such as construction materials, could significantly expand their use of CO<sub>2</sub>. Although CO<sub>2</sub> use is already an important part of creating many of the products society depends on, expanding its use is a viable route to establishing sustainable carbon use for generations to come.

There are four main types of CO<sub>2</sub> use technologies: (1) thermochemical, (2) electrochemical and photochemical, (3) carbonation, and (4) biological conversion.

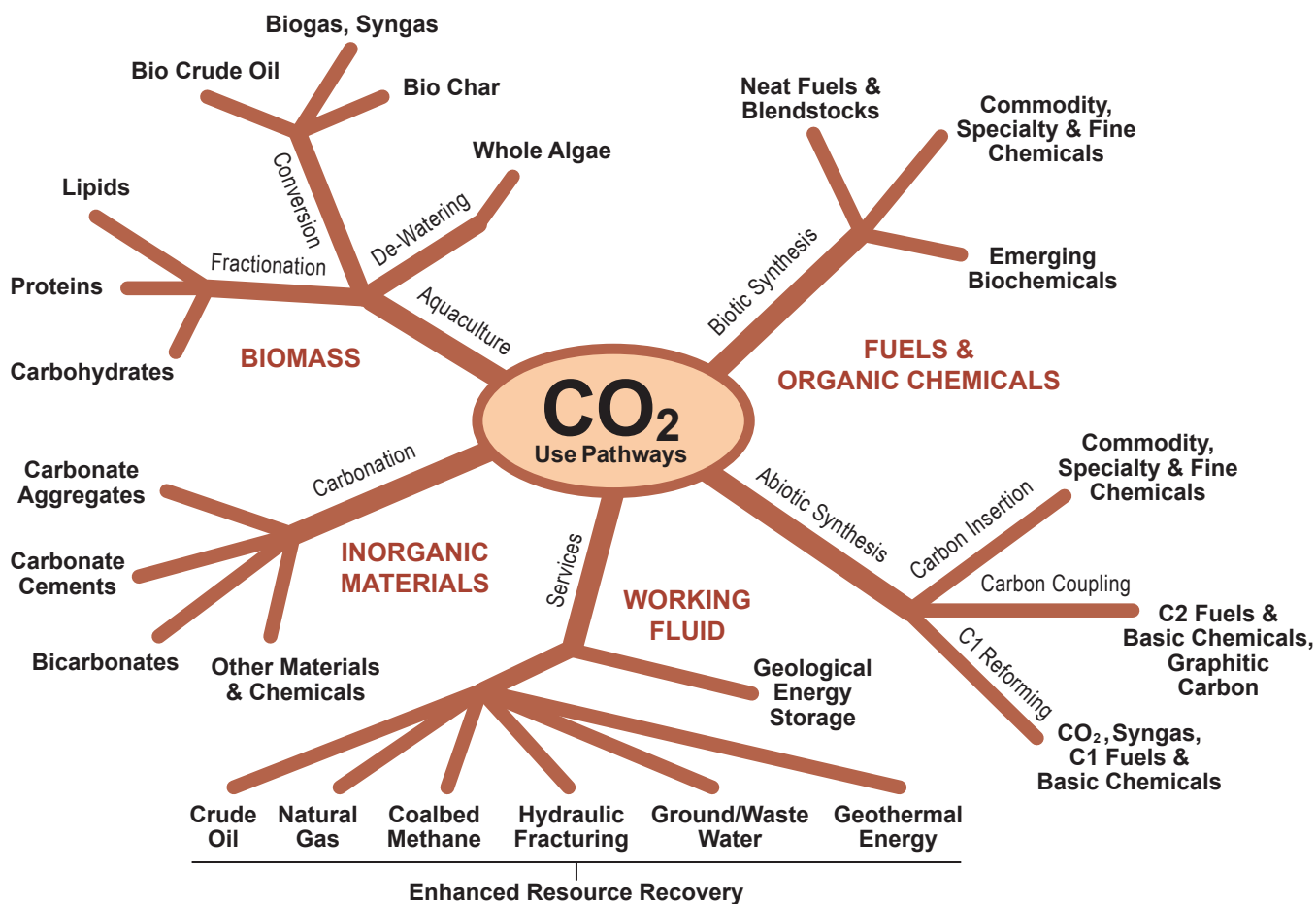
These processes lead to four potential use pathways in which CO<sub>2</sub> is converted into products: (1) fuels and organic chemicals, (2) biomass, (3) inorganic materials, and (4) working fluids (Figure 9-1). Some of these product pathways reduce the carbon intensity of products made with fossil fuels and have a large CO<sub>2</sub> storage potential in the products, chemicals, or fuels that are produced.

While the potential of CO<sub>2</sub> use is compelling, there are significant challenges to overcome before CO<sub>2</sub> use technologies can be deployed at scale. These include:

- *Technology Maturation* — Advancements have been made to understand the fundamental sci-

ence of converting CO<sub>2</sub> into products. Efforts to bridge the gap from concept or laboratory scale to commercial-scale viability are required. Most CO<sub>2</sub> use technologies are at a low level of technical maturity and will need significant research, development, and demonstration (RD&D) to progress.

- *Costs and Energy Efficiency* — One of the fundamental challenges of CO<sub>2</sub> use is that the activation and conversion of CO<sub>2</sub> to chemicals, fuels, and materials requires significant amounts of energy. Thus, at-scale deployment of CO<sub>2</sub> use technologies will depend on technology advancement and the availability of affordable, renewable energy—or alternative forms of low-carbon energy—and inexpensive, clean hydrogen. This is becoming a more realistic proposition because renewable electricity is now at a competitive level with fossil power in many markets, but it may still be years or decades before commercial-scale deployment is possible.
- *Permanence and Indirect Impacts* — The permanence of carbon used in products is an important factor in determining the net environmental impact of CO<sub>2</sub> use. For example, beverage companies purchase CO<sub>2</sub> for carbonating soda but, as soon as the can is opened, the CO<sub>2</sub> is released. If the CO<sub>2</sub> used for carbonation were captured from an industrial source and displaced geologically extracted CO<sub>2</sub>, there would still be an indirect benefit for displacing geologic carbon. It is for this reason that quality life-cycle analyses will be critical in determining the net carbon reduction potential of any CO<sub>2</sub> use technologies. The need to account for permanence and indirect impacts



Source: JM Energy Consulting, Inc, 2019.

**Figure 9-1.** CO<sub>2</sub> Use Pathways

necessitates development of accurate and rigorous life-cycle analysis methodologies or standards.

Although there are several use pathways, CO<sub>2</sub> use alone is insufficient to dramatically reduce CO<sub>2</sub> emissions in the next couple of decades because the amount of CO<sub>2</sub> emitted from all sources greatly exceeds the quantity of carbon-sequestering products currently produced, even concrete. In addition, most use technologies are at a relatively low technology readiness level, and it takes about two decades to develop and commercialize capital-intensive energy and environmental processes.

Increased investment in fundamental research and commercialization support is essential to expedite the pace at which CO<sub>2</sub> use technologies would be ready for commercial-scale deployment. However, the potential of CO<sub>2</sub> use to decrease CO<sub>2</sub>

emissions is impossible to quantify at this stage of development. Furthermore, the timeline to market and scale of CO<sub>2</sub> use opportunities is likely to differ across the United States, Europe, and Asia due to competing factors such as technological development, proximity to markets, and access to low-cost renewable energy or hydrogen.

Progressing CO<sub>2</sub> use options offers synergies if it is done in parallel with other carbon capture and storage (CCS) and energy storage development activities. CCS is necessary to provide the large-scale reductions in emissions that are needed in the next two decades. The early stage development of CO<sub>2</sub> use in various products could accelerate the deployment of CO<sub>2</sub> geological storage by offsetting the cost of CCS and CO<sub>2</sub> transport with end-product revenues. Also, converting CO<sub>2</sub> to high-energy density or high-value chemicals, fuels, and materials using excess renewable energy to provide a wide range of marketable



products would provide an alternative to today's limited energy storage capacity. This could offer a type of seasonal storage of renewable energy.

CO<sub>2</sub> use may appeal to society more readily than other aspects of carbon capture, use, and storage (CCUS), smoothing the pathway to public acceptance. For example, a mattress made with CO<sub>2</sub> captured from a cement plant could be more sustainable, or green, than alternative means of manufacturing that mattress. CO<sub>2</sub> use technologies might present a unique means of entering the global marketplace in the same way as have organic foods and green products, such as shoes and clothing made of recycled plastics. Early introduction of CO<sub>2</sub> use opportunities could improve public awareness and acceptance of CCUS as a method to reduce CO<sub>2</sub> emissions in the next couple of decades.

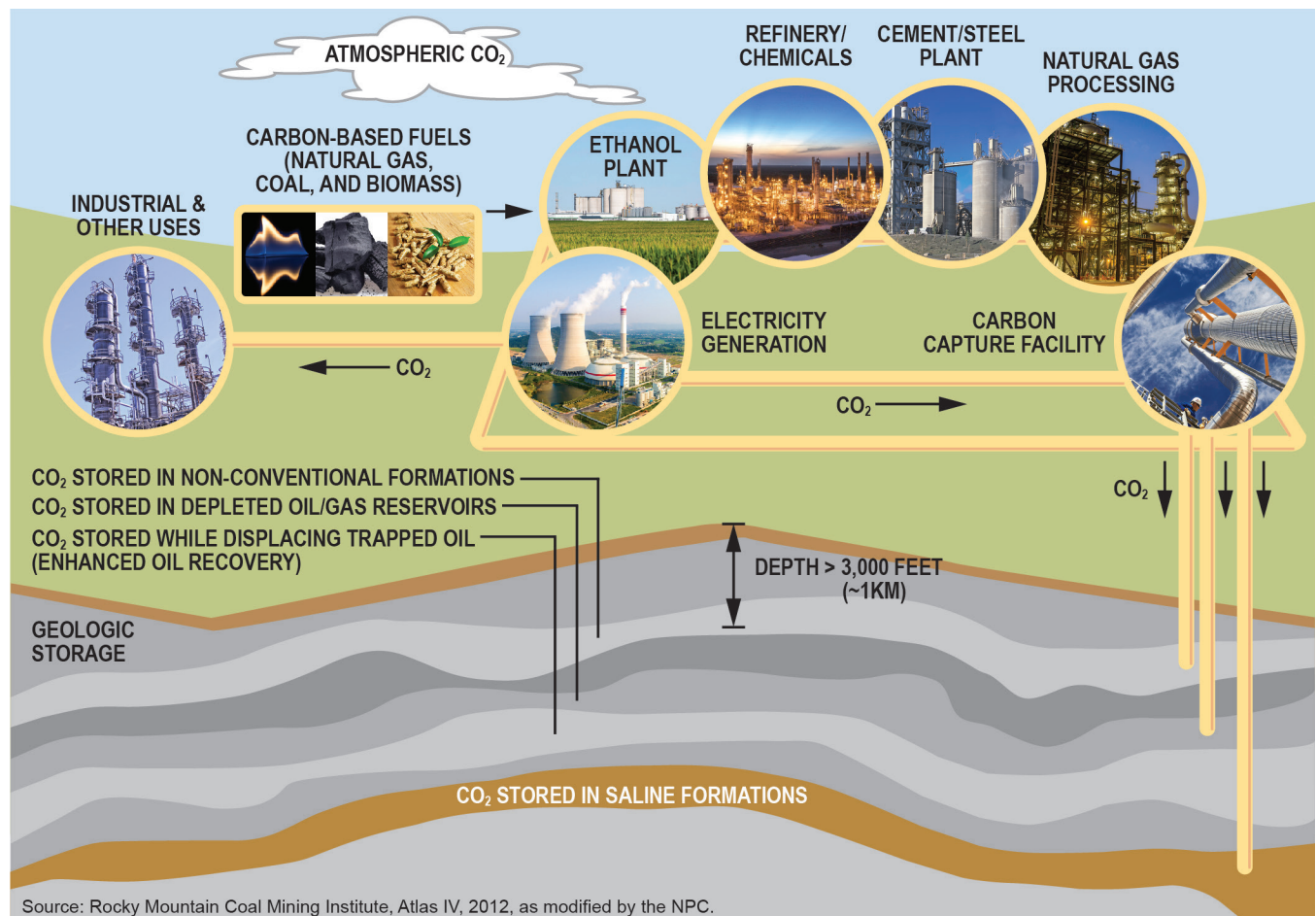
CO<sub>2</sub> use can play a unique and important role in carbon management and progressing national

CO<sub>2</sub> emissions reduction objectives. CO<sub>2</sub> use technologies offer a range of opportunities to create products from CO<sub>2</sub> emissions over the long term, but multiple challenges must be addressed before these technologies can be employed at scale. CO<sub>2</sub> use has the potential to drive technology disruption and has a role to play in delivering negative emissions.

This chapter discusses the main CO<sub>2</sub> use pathways, the potential areas of application of CO<sub>2</sub> use, and priority topics for RD&D.

## II. WHAT IS CO<sub>2</sub> USE?

CCUS, including transport, combines several processes and technologies to reduce the level of CO<sub>2</sub> emitted to the atmosphere or remove CO<sub>2</sub> from the air. The CCUS process, as shown in Figure 9-2, involves the capture (separation and purification) of CO<sub>2</sub> from stationary sources so that it can be transported to a suitable location



Source: Rocky Mountain Coal Mining Institute, Atlas IV, 2012, as modified by the NPC.

**Figure 9-2.** Supply Chain for Carbon Capture, Use, and Storage

where it is converted into useable products or injected deep underground for safe, secure, and permanent storage.

Carbon is one of the most abundant elements on Earth. Its use in various forms has been essential to modern society and the world's economy. Examples of the application of carbon in the economy include fuels, fertilizers, polymers, industrial chemicals, building materials, carbon nanotubes, and many others. It would be difficult to find any materials and products that do not contain carbon or have not resulted in CO<sub>2</sub> emissions during production or utilization.

Unfortunately, CO<sub>2</sub> cannot be burned to generate heat or energy, so it is described as having a low accessible chemical energy—it is chemically inactive. Thus, CO<sub>2</sub> requires a relatively large amount of energy to convert it into products that contain a higher energy. It is these higher-energy products, such as fuels, that can be burned to emit heat. Furthermore, most of these higher-energy products require hydrogen as a co-reactant, and this hydrogen should be produced via a more sustainable process if the carbon intensity of the final product is to be reduced.

CO<sub>2</sub> use technologies convert CO<sub>2</sub> into products via chemical reactions or biological conversions. There are four main types of CO<sub>2</sub> use technologies: (1) thermochemical, (2) electrochemical and photochemical, (3) carbonation, and (4) biological conversion. There is a wide range of potential CO<sub>2</sub> use technology pathways and products that have been identified, each of which is being actively researched. Some of these product pathways reduce the carbon intensity of products made with fossil fuels and have a large CO<sub>2</sub> storage potential in the products, chemicals, or fuels that are produced. For example, the current production of construction materials, such as cement, results in large CO<sub>2</sub> emissions, but innovative cement production using CO<sub>2</sub>, or carbonates produced using CO<sub>2</sub>, could significantly reduce the net CO<sub>2</sub> emissions in the construction industry while storing CO<sub>2</sub> in the form of buildings.

Most CO<sub>2</sub> use technologies are at a low technology readiness level (TRL) and will need substantial research, development, and demonstration (RD&D) funding to progress. It takes

about two decades to develop and commercialize capital-intensive energy and environmental processes. Thus, investment in CO<sub>2</sub> use RD&D funding and commercialization support is essential to expedite the use of CO<sub>2</sub> as a substitute feedstock<sup>1</sup> for traditional extractive single-use sources.

### III. CO<sub>2</sub> USE TECHNOLOGY PATHWAYS AND POTENTIAL PRODUCT OPTIONS

The CO<sub>2</sub> use technologies described in this chapter are divided into four pathways, or categories, based on the reactions involved and their TRL. As shown in Table 9-1, each technology is at a different stage of development and has its own attributes and commercialization potential.

Figure 9-3 displays the technology readiness level of the four main types of use technologies listed in Table 9-1. Each technology pathway on the figure is assigned a TRL range (right vertical axis) that represents its stage of technical development (left vertical axis). The stages of technical development include basic research, development and demonstration, and deployment. The higher the TRL level, the closer the technology is to commercial readiness and subsequent deployment. Most CO<sub>2</sub> use technologies are relatively immature, yet each use category displays a range of TRLs. This is indicative of the challenges and range of opportunities for advancement that may exist across these technology pathways.

#### A. Thermochemical CO<sub>2</sub> Conversion

Thermochemical CO<sub>2</sub> conversion refers to a myriad of high-temperature reactions—such as catalytic hydrogenation, reforming, and oxidation—that produce a range of useful hydrocarbon products. The types of products include olefins (C<sub>2</sub>–C<sub>4</sub>), paraffins (C<sub>5</sub><sup>+</sup>), aromatics, alcohols, organic carbonates, carboxylic acids, and a wide range of polymers. Almost every thermochemical reaction requires the use of catalysts for the reaction to proceed at a reasonable rate, and CO<sub>2</sub> plays varying roles in the different reaction pathways.

<sup>1</sup> Feedstock means that the carbon dioxide is used as a starting material for organic syntheses.

Technology Pathway	Potential Products	Attributes	Technology Readiness Level
Thermochemical	Chemicals, materials, and fuels	Can use abundant natural gas in the United States	2–5
Electrochemical and photochemical	Chemicals, materials, and fuels	Can use the excess renewable energy	1–4
Carbonation and cement	Construction materials, specialty materials (e.g., fillers)	Offers great permanency	5–8
Biological	Chemicals and fuels	Permanency depends on product; slower inherent kinetics than alternative use pathways	3–9

**Table 9-1.** Current Status of CO<sub>2</sub> Use Technologies

The CO<sub>2</sub> can be used as a feedstock, a co-reactant, or a mild oxidant.<sup>2</sup>

There have been remarkable advances using new catalysts to increase the selectivity<sup>3</sup> of CO<sub>2</sub> hydrogenation into desired products—either hydrocarbons or alcohol. These include:

- New bimetallic catalysts for CO<sub>2</sub> conversion to olefins and C<sub>5</sub>+ hydrocarbons (i.e., iron-cobalt [Fe-Co] and iron-copper [Fe-Cu] on various supports) or to methanol (i.e., palladium-copper [Pd-Cu])
- New metal-oxide hybrid catalysts (i.e., Fe<sub>3</sub>O<sub>4</sub>-FeC<sub>n</sub>/ZSM-5)
- New binary oxide-based multicomponents or hybrid catalysts (i.e., In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/ZSM-5 and ZnO-ZrO<sub>2</sub>/ZSM-5 hybrids) for CO<sub>2</sub> hydrogenation to energy-rich hydrocarbon and alcohol products in the past decade.

2 The chemical conversion of CO<sub>2</sub> to chemicals and fuels has been extensively discussed in several reports:

U.S. Department of Energy. (2018). “Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage,” Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts’ Workshop, September 2017, Houston.

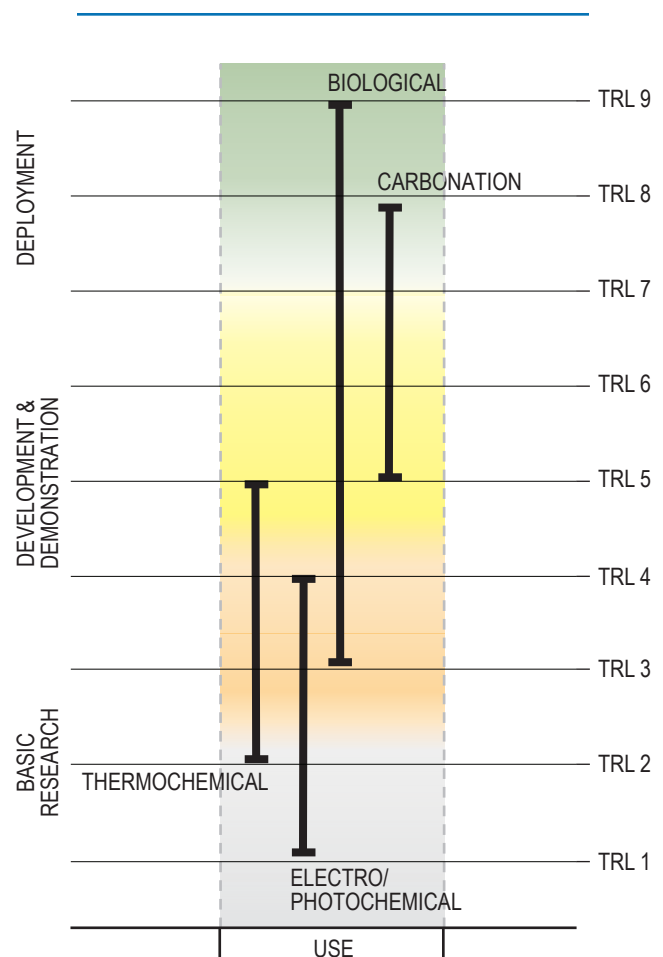
Global CO<sub>2</sub> initiative, “Global Roadmap for Implementing CO<sub>2</sub> Utilization,” doi: 10.3998/2027.42/146529.

National Academies of Sciences, Engineering, and Medicine. (2019). *Gaseous Carbon Waste Streams Utilization: Status and Research Needs*. Washington, DC: The National Academies Press, <https://doi.org/10.17226/25232>.

National Coal Council. (2016). “CO<sub>2</sub> building blocks: Assessing CO<sub>2</sub> utilization options.” Washington, DC. <https://www.nationalcoalcoalouncil.org/studies/2016/NCC-CO2-Building-Blocks-Executive-Summary.pdf>.

3 Selectivity is the preferential outcome of a chemical reaction over a set of possible alternative reactions.

Computational research has contributed significantly to developing a fundamental understanding of surface interactions and reaction pathways.



Source: Figure ES-18.

**Figure 9-3.** Technology Readiness Level (TRL) Ranges for CCUS Use Technologies

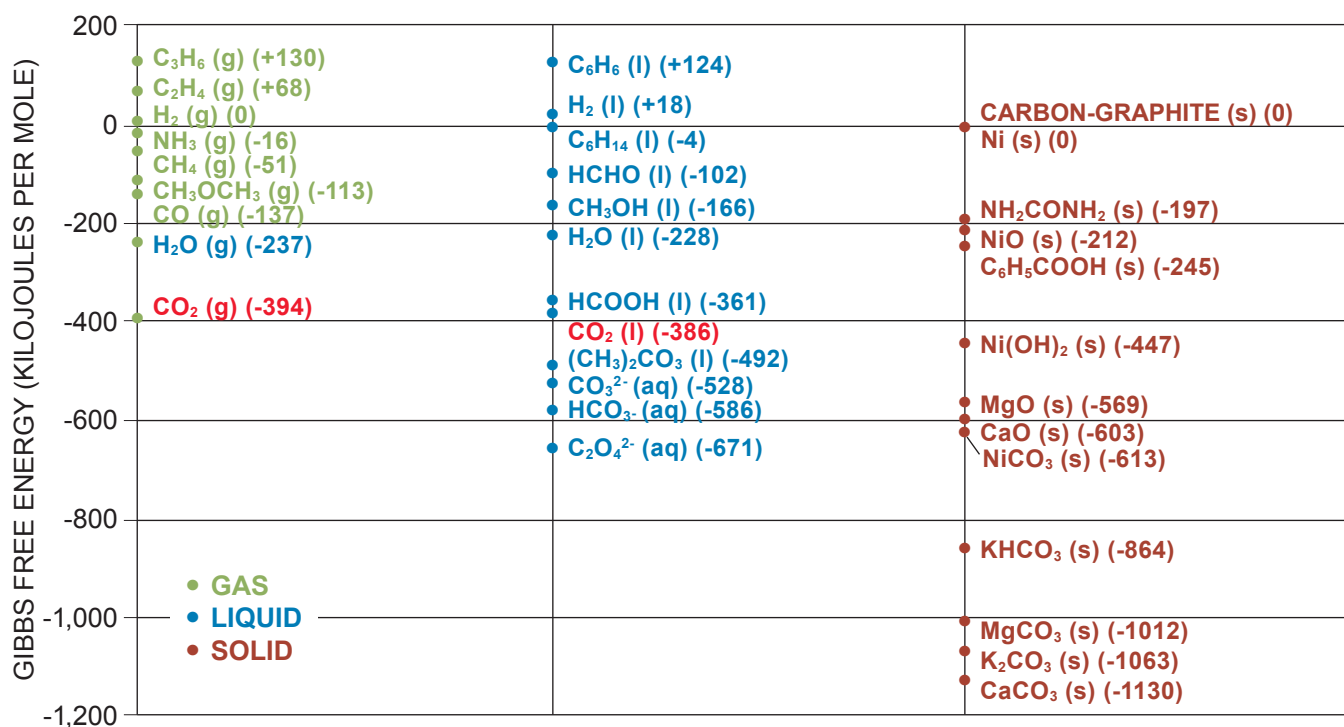
One of the major challenges associated with CO<sub>2</sub> conversion is the thermodynamic stability of the CO<sub>2</sub> molecule itself (Figure 9-4).<sup>4</sup> This refers to the fact that CO<sub>2</sub> typically needs to be reacted with high-energy reagents such as hydrogen (H<sub>2</sub>) or epoxides for processes to be thermodynamically favorable. Figure 9-4 uses Gibbs free energy in kilojoules per mole (kJ/mole) to illustrate that the lower the Gibbs free energy, the lower the energetic value of the gases, liquids, and solids shown. Thus, to make products that have a higher Gibbs free energy than CO<sub>2</sub>, additional low-carbon intensity energy inputs will be required.

Generation of these reagents, especially of H<sub>2</sub>, requires large amounts of fossil fuel resources, so they lack the net CO<sub>2</sub> benefit that would be desired from a life-cycle emissions perspective. For net CO<sub>2</sub> emissions reductions to occur from thermochemical processes involving CO<sub>2</sub> and H<sub>2</sub>, the source H<sub>2</sub> must have a low-carbon footprint.

For H<sub>2</sub> to have a low-carbon footprint, it must be generated from a renewable source, such as electrolysis of water, using electricity generated from renewable or fossil fuel energy from carbon neutral sources.

Current examples of large-scale products that are made commercially from CO<sub>2</sub> are limited, though there are many product pathways at a smaller scale. For example, CO<sub>2</sub> is combined with ammonia to make urea in a process that uses some of the CO<sub>2</sub> generated during the production of H<sub>2</sub> from natural gas for ammonia synthesis. Although urea is one of the largest CO<sub>2</sub> applications—annual global CO<sub>2</sub> demand in 2017 was 157 million tonnes—using CO<sub>2</sub> to produce urea does not permanently sequester the CO<sub>2</sub>. Methanol is industrially produced from synthesis gas (syngas), composed of carbon monoxide (CO) and H<sub>2</sub>, but up to 30% of the CO<sub>2</sub> can be incorporated into the starting gas stream and is also converted to product. Systems for the direct hydrogenation of CO<sub>2</sub> to methanol are also operating industrially but produce only a small fraction of the total methanol produced globally and are not cost competitive unless there are strong financial

4 Song, C. S., "Global Challenges and Strategies for Control, Conversion and Utilization of CO<sub>2</sub> for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing," *Catalysis Today*, 2006, 115, 2–32.



Source: Song, C.S., "Global Challenges and Strategies for Control, Conversion and Use of CO<sub>2</sub> for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing," *Catalysis Today*, 2006, 115, 2–32.

**Figure 9-4.** Thermodynamic Considerations for Converting CO<sub>2</sub> to Chemicals and Fuels



incentives for CO<sub>2</sub> use. Over the last decade several polymers have begun to be produced from CO<sub>2</sub>, offering another pathway of potentially scalable relevance.

The range of chemicals that are produced from CO<sub>2</sub> could be increased if more efficient technologies were developed, low-carbon energy sources were available, and financial incentives were in place. Improvements in technology and financial incentives could increase the market share of chemicals that are produced from CO<sub>2</sub> capture because they must compete with less expensive non-CO<sub>2</sub> based routes. For practical application, integration of the conversion processes with a more efficient and geographically compact CO<sub>2</sub> capture process may be preferred for chemical processing.<sup>5</sup>

## 1. Technology to Market Experience

There are a few examples of thermochemical conversion of CO<sub>2</sub> into products (fuels, methanol, and polyurethane foam) that are currently available in the market or are approaching market availability.

In Dresden, Germany, Sunfire built a pilot plant from 2013 to 2014 that can produce 160 liters (~1 barrel) of hydrocarbons a day from CO<sub>2</sub> using a three-stage process: (1) H<sub>2</sub> production by electrolysis with renewable electricity, (2) CO<sub>2</sub> hydrogenation to CO, and (3) Fischer-Tropsch conversion of the CO to generate hydrocarbons.<sup>6</sup> Sunfire reported an electricity-to-fuel carbon efficiency of 70%.

In July 2017, Sunfire announced a plan to build the first commercial plant to produce an environmentally friendly crude oil substitute called Blue Crude. The plant will be built in Heroya, Norway, in 2020 and have an electric capacity of 20 MW, producing 8,000 tonnes of Blue Crude per year. This should be enough to provide fuel for 13,000 cars per year. The Blue Crude target price is less than €2 per liter. When the Heroya plant is run-

ning at full capacity, production of Blue Crude will prevent 21,000 tonnes of CO<sub>2</sub> emissions that producing the fuels from fossil fuel would have generated. Currently, the rate at which the fuel can be produced is slow and many more plants that are the same size as the Heroya plant would be required for this CO<sub>2</sub> use technology to be suitable for widespread adoption. The cost of the fuel is also higher than conventional fuel sources.

In Iceland, Carbon Recycling International (CRI) built a CO<sub>2</sub>-to-methanol plant in Svartsengi that was completed in 2012. The CO<sub>2</sub> is captured from flue gas released by a geothermal power plant located next to the CRI facility. The plant uses electricity to make H<sub>2</sub>, which is used for the catalytic hydrogenation of CO<sub>2</sub> to methanol. In 2015, CRI expanded the plant from a capacity of 1.3 million liters per year to more than 5 million liters per year. The plant now recycles 5.5 thousand tonnes of CO<sub>2</sub> per year that would otherwise be released into the atmosphere.

Unfortunately, the process is economically feasible only in Iceland for three reasons: (1) the availability of low-cost electricity required to generate the H<sub>2</sub>, (2) the high concentration of CO<sub>2</sub> in the flue gas (85% to 90%), which substantially lowers the cost of CO<sub>2</sub> compared with more traditional flue gas streams that contain lower amounts of CO<sub>2</sub>, and (3) the European Union requirement that a certain fraction of liquid fuels, such as methanol, must be produced in a sustainable fashion. At this stage, it would not be economically feasible to implement this CO<sub>2</sub> use technology in other locations, and the scale of the plant is also significantly smaller than most traditional methanol production plants.

Covestro has developed and commercialized a new flexible polyurethane foam that incorporates a CO<sub>2</sub>-based polyol made by copolymerization of CO<sub>2</sub> and propylene. The foam is used in mattresses and was first released on the market in 2016. The polyol contains a CO<sub>2</sub>-content of approximately 20%, which is obtained from a nearby ammonia plant. The production of the polyol still results in net emissions of CO<sub>2</sub>, but emissions are reduced due to the use of CO<sub>2</sub> as a feedstock compared with the traditional non-CO<sub>2</sub> based route to these polyols. From a life-cycle perspective, additional benefits from replacing part of the propylene

5 Ma, X. L., Wang, X. X., and Song, C. S., "Molecular Basket: Sorbents for Separation of CO<sub>2</sub> and H<sub>2</sub>S from Various Gas Streams." *Journal of American Chemical Society*, 2009, 131 (16), 5777–5783.

6 Fischer-Tropsch process is a set of chemical reactions that changes a mixture of carbon monoxide gas and hydrogen gas into liquid hydrocarbons like gasoline or kerosene.



oxide with polyol are reflected in lower toxicity, eutrophication, and acidification.<sup>7,8</sup> The scale at which the CO<sub>2</sub>-derived polyols are produced is approximately 60 times smaller than conventional polyol plants, but plans are in place to build a larger plant that is only three times smaller than a conventional plant. As of 2018, the new process appears to be a commercial success, but longer-term evaluation is required.

## 2. Product Options

There are a range of products that can be formed from CO<sub>2</sub>. For example, the hydrogenation of CO<sub>2</sub> can produce olefins, liquid hydrocarbons, including aromatics, syngas, methanol, dimethyl ether, formic acid, and other chemicals. In general, these products are currently produced using petroleum, natural gas, or syngas (CO+H<sub>2</sub>) using processes that have been optimized to operate with low profit margins. Nevertheless, the catalytic hydrogenation of CO<sub>2</sub> using H<sub>2</sub> produced from a renewable energy source could significantly contribute to the sustainable production of chemicals, materials, and fuels if efficient and selective processes are developed. The major challenges that need to be resolved for the development of new technology for CO<sub>2</sub> conversion are associated with the thermodynamic and kinetic stability of CO<sub>2</sub>.

One of the simplest products that can be made from CO<sub>2</sub> is carbon monoxide (CO). This can be achieved using the reverse water-gas shift process. Specifically, H<sub>2</sub> and CO<sub>2</sub> is converted into CO and water (H<sub>2</sub>O), though the process requires heat to proceed.

Another potentially important C1 product that can be synthesized from CO<sub>2</sub> is formic acid. Formic acid is currently produced through the reaction of CO with methanol to generate methyl formate. Although formic acid has a relatively small market size—about 700 kilotonnes per year glob-

ally—new markets are being explored, such as its use as an intermediate and a hydrogen carrier.

Methanol is a highly desirable target from CO<sub>2</sub> hydrogenation because it has potential as a chemical building block and a fuel. It has been recognized that the presence of CO<sub>2</sub> in or addition of CO<sub>2</sub> to the feed gas of CO and H<sub>2</sub> is beneficial for methanol synthesis over commercial Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst. Many studies have reported on the improvement of the Cu-ZnO-based catalysts with various promoters and modifiers. However, in the past 5 years, there has been substantial progress in developing fundamentally new catalyst formulations for CO<sub>2</sub> hydrogenation to methanol.

Aromatics are important for the production of chemicals and polymers and constitute about one-third of the market for commodity petrochemicals. However, the production of aromatics relies heavily on petroleum, so CO<sub>2</sub> hydrogenation to aromatics is a promising alternative route that has emerged for carbon mitigation purposes.

The direct incorporation of CO<sub>2</sub> into polymers is an area where some technology is at a commercial stage and other efforts are still in the research phase. The possibility of using CO<sub>2</sub> as feedstock for polymers, followed by circular management practices (e.g., increased recycling), provide the potential to keep the CO<sub>2</sub> out of the atmosphere for longer periods of time compared to chemicals or fuels. Polycarbonates, which have applications as a component in polyurethanes as well as in the electronics, transport, and construction industries, are the major type of polymer produced from CO<sub>2</sub>.

Two types of polycarbonates can be produced through the copolymerization of CO<sub>2</sub> with epoxides by sequentially alternating one molecule of CO<sub>2</sub> and one molecule of epoxide that only contains carbonate groups, or using a statistical arrangement containing ether linkages that are generated when two ring-opened epoxides are adjacent to each other. Statistical polycarbonates, which are often referred to as polyether carbonates, have more desirable properties for industrial applications because alternating polycarbonates have low glass transition temperatures. Commercial processes, however, have already been developed to form both alternating

7 von der Assen, N., and Bardow, A., "Life cycle assessment of polyols for polyurethane production using CO<sub>2</sub> as feedstock: insights from an industrial case study," *Green Chemistry*, 2014;16(6):3272-80.

8 Fernández-Dacosta, C., Van Der Spek, M., Hung, C. R., Oregionni, G. D., Skagestad, R., Parihar, P., et al., "Prospective techno-economic and environmental assessment of carbon capture at a refinery and CO<sub>2</sub> utilisation in polyol synthesis," *Journal of CO<sub>2</sub> Utilization*, 2017; 21:405-22.

polycarbonates and polyether carbonates. These are not yet conducted at a significant industrial scale because the products tend to be for niche applications and there are many opportunities to develop new polymers with unique properties from CO<sub>2</sub>. This may be achieved by increasing the range of epoxides that can be efficiently copolymerized with CO<sub>2</sub> or developing systems that are derived from renewable epoxide feedstocks. Homogeneous catalysis likely provides the best initial opportunity for making progress in this area due to the control it can exert over selectivity.

Carboxylic acids, several of which are produced on a very large scale, have numerous industrial applications and could, in principle, be prepared by inserting CO<sub>2</sub> into a carbon-hydrogen (C–H) bond of a hydrocarbon. In most cases, however, inserting CO<sub>2</sub> into a C–H bond is thermodynamically unfavorable. Thus, most catalytic processes for generating carboxylic acids from CO<sub>2</sub> and bases are performed in the presence of a base. Currently, catalytic systems to produce acrylic acid, methacrylic acid, benzoic acid, and furan-2,5-dicarboxylic acid have been established. These systems are still in the research phase though, and some of the problems that need to be resolved include low catalyst turnover numbers, the need for expensive stoichiometric additives for thermodynamic reasons, and low reactions rates.

Conversion of CO<sub>2</sub> to carbon products—carbon black, carbon nanotubes, and carbon nanofibers, all via the patented Noyes Process—is being developed by Solid Carbon Products in Provo, Utah. Their process uses either hydrogen or natural gas as the energy source to catalytically convert CO<sub>2</sub> to elemental carbon materials and nanomaterials. Carbon black is a commodity material that is used in tires and composites.

## B. Electrochemical and Photochemical CO<sub>2</sub> Conversion

Electrochemical and photochemical CO<sub>2</sub> conversion uses electrons and protons to activate CO<sub>2</sub> to produce a wide array of products. For electrochemical conversion, electricity is used to provide energy for the CO<sub>2</sub> conversion reaction. The electrochemical pathway can employ electricity from various sources, including renewable energy

from solar and wind, which provides flexibility in energy sourcing. The photochemical conversion pathway uses sunlight to convert CO<sub>2</sub> and water into solar fuels using photochemistry.

One of the main challenges of both electrochemical and photochemical conversion of CO<sub>2</sub> is its competition with the hydrogen evolution reaction that has a similar reduction-oxidation (redox)<sup>9</sup> potential as the CO<sub>2</sub> reduction reaction. As a result, substantial effort is being dedicated to developing reaction systems that favor the conversion of CO<sub>2</sub> to chemicals and fuels.

Electrochemical conversion of CO<sub>2</sub> (CO<sub>2</sub> electrolysis) is capable of producing a wide array of products. Utilizing electrochemical reduction reactions, CO<sub>2</sub> has been successfully converted into both single carbon (C<sub>1</sub>) and multicarbon products (C<sub>2</sub><sup>+</sup>). The simplest reduction product generated from CO<sub>2</sub> is CO, which has been well researched and is the closest to being commercially available. In addition, different designs of flow reactors have been developed to produce CO with an electric efficiency of more than 90%. Figure 9-5 shows various catalytic pathways (both thermochemical and electrochemical) to produce sustainable fuels and chemicals using carbon-free energy sources.

The reactor design that produces the highest performance is the solid-oxide reactor (SOE), which can produce nearly pure CO at rates of 2 cubic meters per hour. Even though SOEs demonstrate very good performance operating at powers in the kilowatt scale, they need to operate at very high temperatures of greater than 1,000 K (727C) to overcome the resistance from the ceramic electrode. Ambient temperature electrolyzers (ATEs) provide another option for producing CO without the need for heating to such extreme levels. State-of-the-art ATEs using a silver cathode, and either dissolved CO<sub>2</sub> or humidified CO<sub>2</sub>, produce CO at high efficiencies but suffer from suboptimal performance, partially due to energy losses in the anode. A strategy to overcome these

<sup>9</sup> Redox is a type of chemical reaction in which the oxidation states of atoms are changed. Redox reactions are characterized by the transfer of electrons between chemical species, most often with one species (the reducing agent) undergoing oxidation (losing electrons) while another species (the oxidizing agent) undergoes reduction (gains electrons).





Although these reactors have shown promising results, they are still in the early stages of development and far from commercial application.

Photochemical conversion is the reduction of CO<sub>2</sub> via photocatalysis, where sunlight is used to convert CO<sub>2</sub> and water into solar fuels using photochemistry. Photochemistry relies on photon-induced transitions between the electronic states of the catalyst and consequent interaction with the molecular orbitals of adsorbed reactant species. Both processes occur in the same material that serves as the photocatalyst.

While indirect approaches such as electrochemistry rely on an alternative energy input (electricity) produced by an external device (photovoltaic cell or other low-carbon electrical power source) and the resulting electrical potential to split the strong double carbon-oxygen bond (C=O), photocatalysis uses light to catalyze the reaction. Photochemical conversion methods provide an advantage over the use of electrochemical methods because there is no need to input energy into the system. A wide array of catalysts has been tested, typically using a solution of CO<sub>2</sub> and water, with the primary products being CO, CH<sub>4</sub>, and CH<sub>3</sub>OH. Some studies have shown production of C<sub>2</sub><sup>+</sup> products, but at much lower rates than the electrochemical methods. Even with the higher selectivity shown with the photochemical approach, reaction rates are still far too low for commercial use. As a result, significant research is necessary to optimize photochemical systems before they will be ready for commercial use.

The complete photochemistry mechanism involves light absorption to induce charge carrier separation, followed by the transport of carriers to the active surface sites for catalytic CO<sub>2</sub> reduction. Photocatalysts are often hybrid materials involving a semiconductor embedded with a metal or metal-oxide co-catalyst (platinum [Pt], palladium [Pd], copper [Cu], ruthenium [Ru], nickel-oxide [NiO<sub>2</sub>], ruthenium-oxide [RuO<sub>2</sub>]) and can include a sensitizing agent to increase light absorption. Nanostructuring strategies have largely dominated the research and development of photocatalysts, and nanoparticle catalysts are favored for their readily tunable surface properties. It has been reported that the use of

high surface area support materials can also offer increased dispersion, stability, and photoresponse of the nanoparticle catalysts, resulting in their improved efficiency and durability. Despite nanostructuring breakthroughs, the principal challenge of photochemistry remains the limited adsorption and use of the solar spectrum by existing photocatalysts.

CO<sub>2</sub> can also be reduced directly via homogeneous photocatalysis. Homogeneous catalysts are typically metal complexes that serve the dual function of light absorber and active site. Because molecular catalysts often rely on expensive and rare metals (like ruthenium [Ru] and rhodium [Rh]), they have limited potential for industrial scaling. Currently, a lack of standardization for reported measurements has impeded proper benchmarking of photocatalytic CO<sub>2</sub> reduction. Formation rates of products remain on the order of micromoles per gram of catalysts per hour ( $\mu\text{mol gcat}^{-1} \text{h}^{-1}$ ).

Emergence of novel carbon-based materials (e.g., graphitic carbon nitride) as photocatalysts is encouraging because these systems can be process-intensified to conduct capture and conversion in one step. Advancement in nanoscience has enabled synthesis of morphology-controlled nanomaterials with tunable properties to enhance light harvesting and energy efficiencies in the system.

There remain several challenges associated with CO<sub>2</sub> use through electrochemical and photochemical approaches. Selectivity and the pace of reaction rates into desired products require improvements before they will become industry or market ready. Also, electrochemical and photochemical systems must address challenges related to the concentration and purity of realistic CO<sub>2</sub> sources (diluted and contaminated), as well as the intermittency of renewable electricity and sunlight. With further research and development, CO<sub>2</sub> electrochemical and photochemical reductions are potentially economical approaches for carbon use.

## 1. Technology to Market Experience

A few examples of electrochemical conversion of CO<sub>2</sub> exist, all of which involve conversion to carbon monoxide. Currently, there are no

equivalent photochemical conversion activities at this scale:

- Opus 12 has developed a PEM-based<sup>10</sup> polymer electrolyte cell that has achieved high selectivity and current density for CO<sub>2</sub> conversion to CO. The team is also pursuing the means to produce other products such as methane, ethylene, and ethanol. The core innovation of the Opus 12 team is their polymer electrolyte membrane electrode assembly that can be substituted for the conventional platinum-coated monoethanolamine (MEA) in a PEM water electrolyzer.
- Haldor Topsoe used a solid-oxide technology to convert CO<sub>2</sub> to CO. However, the operating temperature of this process is high (700°C to 850°C), which limits its range of applicability when integrated with intermittent renewable energy sources. The technology has, however, proven to have high energy efficiency and offer opportunity for waste-heat recovery and heat integration. Haldor Topsoe is marketing a high-temperature electrochemical cell capable of generating CO from CO<sub>2</sub> at a commercial scale.
- Dioxide Materials has developed a low-temperature electrochemical technology and is already marketing this technology for laboratory use.

## 2. Product Options

The electrochemical reduction of CO<sub>2</sub> can proceed through a two-, four-, six-, eight-, twelve-, or eighteen-electron reduction pathway to produce various gaseous products (carbon monoxide, methane, ethylene) and liquid products (formic acid, methanol, ethanol, n-propanol, acetate).<sup>11</sup> Other minor products have also reported including glyoxal, ethylene glycol, acetaldehyde, propionaldehyde, etc.<sup>12</sup>

Similar products can be made via photochemical pathways.

## C. Carbonation and Cement Uses of CO<sub>2</sub>

Carbonation, or carbon mineralization, refers to the inorganic reaction pathway that transforms gaseous CO<sub>2</sub> into solid carbonates, typically in a permanent way, in the form of thermodynamically stable and environmentally benign mineral carbonates. The carbonation of alkaline minerals mimics the natural alteration of calcium- and magnesium-rich rocks as they react with atmospheric CO<sub>2</sub> over geological timescales.<sup>13</sup> Examples of carbon mineralization in nature include the weathering of rocks on the Earth's surface and the underground formation of carbonate rocks such as limestone.

The carbon mineralization reaction occurs very slowly in nature. CO<sub>2</sub> use technologies accelerate the natural weathering process of calcium- and magnesium-bearing minerals and rocks. Alkaline industrial wastes containing high concentrations of calcium and magnesium can also be used for carbon mineralization.

The carbonation pathway can be used to produce more sustainable products, like green construction materials. Cement curing can also use CO<sub>2</sub> instead of steam, which significantly reduces the energy requirement. As a result, a carbon credit can be earned for the CO<sub>2</sub> that is not released during the production of concrete blocks.

It is estimated that the natural reserves of calcium and magnesium silicates near the Earth's surface are enough to store all the CO<sub>2</sub> that could be produced from all the identified fossil fuel reserves that are recoverable.<sup>14</sup> Still, substantial scale up and acceleration of the mineral carbonation reaction through process intensification routes is required if the

<sup>10</sup> PEM stands for proton exchange membrane.

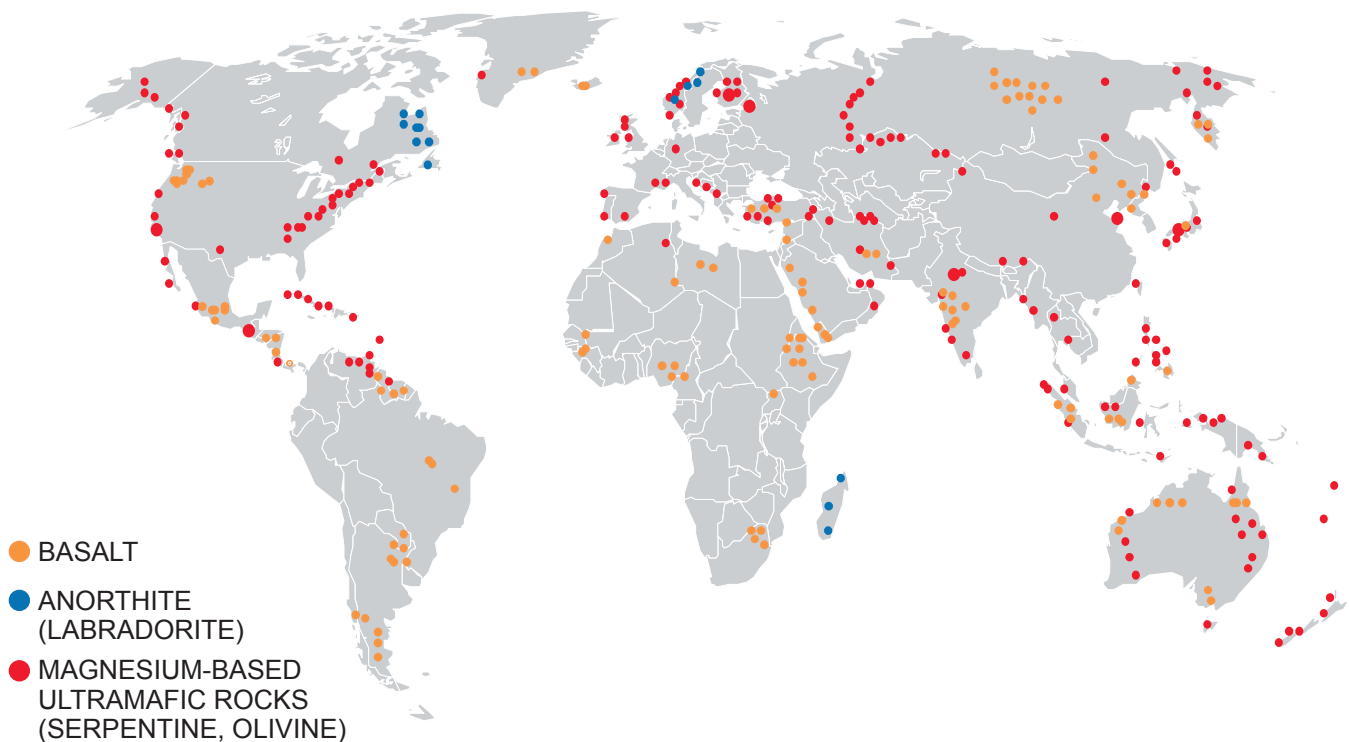
<sup>11</sup> Hori, Y., "Electrochemical CO<sub>2</sub> Reduction on Metal Electrodes," *Modern Aspects of Electrochemistry*, vol. 42 (Springer, 2008).

<sup>12</sup> Kuhl, K. P., Cave, E. R., Abram, D. N., and Jaramillo, T. F., "New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces," *Energy & Environmental Science*, vol. 5, Issue 5, p. 7050-7059, 2012, doi: 10.1039/c2ee21234j.

<sup>13</sup> Serifritz, W. (1990). "CO<sub>2</sub> Disposal by Means of Silicates." *Nature* 345 (6275):486-486. <https://doi.org/10.1038/345486b0>.

<sup>14</sup> Lackner, K. S. (2003). "A Guide to CO<sub>2</sub> Sequestration." *Science*. <https://doi.org/10.1126/science.1079033>.





Sources: Gadikota, G., and Park, A-H. A., "Accelerated Carbonation of Ca- and Mg-Bearing Minerals and Industrial Wastes Using CO<sub>2</sub>," in *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, 1st ed., 2014; and Gadikota, G., "Geo-Chemo-Physical Studies of Carbon Mineralization for Natural and Engineered Carbon Storage" (PhD diss., Columbia University, 2014).

**Figure 9-6.** Global Distribution of Continental Rocks and Minerals with CO<sub>2</sub> Storage Capabilities

rate of CO<sub>2</sub> emissions from industrial sources is to be matched, and if carbonation in an economical and net-positive manner is to be achieved.<sup>15,16,17,18</sup>

In this context, evaluating the potential of carbon mineralization for CO<sub>2</sub> use and storage is important. Several gigatonnes of carbon can be converted in natural geologic materials while 200 Mt to 300 Mt of CO<sub>2</sub> can be converted to calcium and magnesium carbonates in alkaline

industrial residues annually.<sup>19,20</sup> Figure 9-6 shows the availability globally of calcium- and magnesium-bearing, naturally occurring rocks and minerals for carbon mineralization.

Carbon mineralization can also be applied to a variety of industrial waste materials. These materials are typically by-products of high-temperature processes, such as slags and fly ashes, but can also include tailings (waste) from mineral processing operations and other suitable

15 Santos, R. M., and Van Gerven, T. (2011). "Process Intensification Routes for Mineral Carbonation." *Greenhouse Gases: Science and Technology* 1 (4). Wiley Online Library:287–93.

16 Santos, R. M., Verbeeck, W., Knops, P., Rijnsburger, K., Pontikes, Y., and Van Gerven, T. (2013). "Integrated Mineral Carbonation Reactor Technology for Sustainable Carbon Dioxide Sequestration: 'CO<sub>2</sub>Energy Reactor,'" in *Energy Procedia*. <https://doi.org/10.1016/j.egypro.2013.06.513>.

17 McCulloch, S. (2016). "20 Years of Carbon Capture and Storage: Accelerating Future Deployment." Paris: International Energy Agency.

18 Bourgeois, F., Julcour-Lebigue, C., Cassayre, L., Bailly, F., Cyr, M., and Touzé S. (2018). "Guiding Mineralization Process Development with Geochemical Modelling." *Proceedings of the 14th International Conference on Greenhouse Gas Control Technologies, GHGT-14*, 21-25 October 2018, Melbourne, Australia.

19 Bobicki, E. R., Liu, Q., Xu, Z., and Zeng, H. (2012). "Carbon Capture and Storage Using Alkaline Industrial Wastes." *Progress in Energy and Combustion Science*, <https://doi.org/10.1016/j.peccs.2011.11.002>.

20 Sipilä, J., Teir, S., and Zevenhoven, R. (2008). "Carbon Dioxide Sequestration by Mineral Carbonation – Literature Review Update 2005–2007." *Åbo Akademi Univ., Heat Engineering Lab*. <https://doi.org/10.1080/00908310600628263>.

waste materials.<sup>21,22,23,24,25</sup> These wastes are generally inorganic, alkaline, and possess a high amount of calcium or possibly magnesium. The advantage of calcium waste is that it has greater reactivity due to the lower Gibbs free energy of the carbonation reaction.

Industrial waste materials also have several advantages compared to natural minerals. They tend to be generated in industrial areas near large CO<sub>2</sub> point sources, often have low to negative market prices, and possess higher reactivities because of their inherent chemical instability. Wastes are also generally available in particulate form, which is favorable in terms of specific surface area.

Other benefits in addition to CO<sub>2</sub> conversion to carbonates include stabilization of leaching, basicity, and structural integrity that further enable the valorization of waste materials, either via reduced waste treatment or landfilling costs, or the production of marketable products. The reduction of industrial waste stockpiling reduces our reliance on land resources. However, the availability of these alkaline industrial residues, which is significantly lower than that of natural minerals, and the relative amounts of calcium and magnesium in these residues dictates the extent to which CO<sub>2</sub> can be converted to calcium and magnesium carbonates. Figure 9-7 shows various carbon mineralization pathways utilizing different feedstocks to fix CO<sub>2</sub> into value-added solid carbonate products. Efforts to colocate processes for CO<sub>2</sub> conversion to calcium and magnesium carbonates with the sources of alkaline industrial residues need to consider the relative abundance of CO<sub>2</sub> emis-

sions and the quantity of alkaline industrial residues.

Figure 9-8 shows the annual U.S. CO<sub>2</sub> emission rates produced from each industrial sector and the corresponding co-generated alkaline industrial residues. These data suggest that the potential for carbon mineralization using alkaline industrial residues produced in the mining sector to exceed the sector's CO<sub>2</sub> emissions, unlike in the case of power generation, iron and steel production, and cement and aluminum production. However, additional factors such as conversion efficiency, reactor design (e.g., heat input and grinding requirements), and material handling must be investigated on a case-by-case basis to determine the relative carbon footprint and life cycle of each proposed project.

One issue is that mineralization of natural minerals or alkaline wastes does not produce only carbonates. The dissolution process yields a mixture of phases as the dissolution of calcium (Ca) and magnesium (Mg) is generally congruent with the other elements present inside the mineralization feedstock. Mineralization of silica-bearing feedstocks can produce amorphous silica, which can be valuable. Invariably, mineralized products will bear some initial feedstock particles that have not undergone mineralization. Moreover, the dissolution of mineralization feedstocks will liberate metals in the leached solution that could also be concentrated via purification techniques and valorized. The Mission Innovation report published in 2018 introduces the concept of enhanced metal recovery, which uses mineralization specifically for extraction of valuable metals from mineralization feedstocks.<sup>26</sup> A critical mass

21 Gadikota, G., and Park, A-H. A. (2014). "Accelerated Carbonation of Ca- and Mg-Bearing Minerals and Industrial Wastes Using CO<sub>2</sub>." *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, First Edition, <https://doi.org/10.1016/B978-0-444-62746-9.00008-6>.

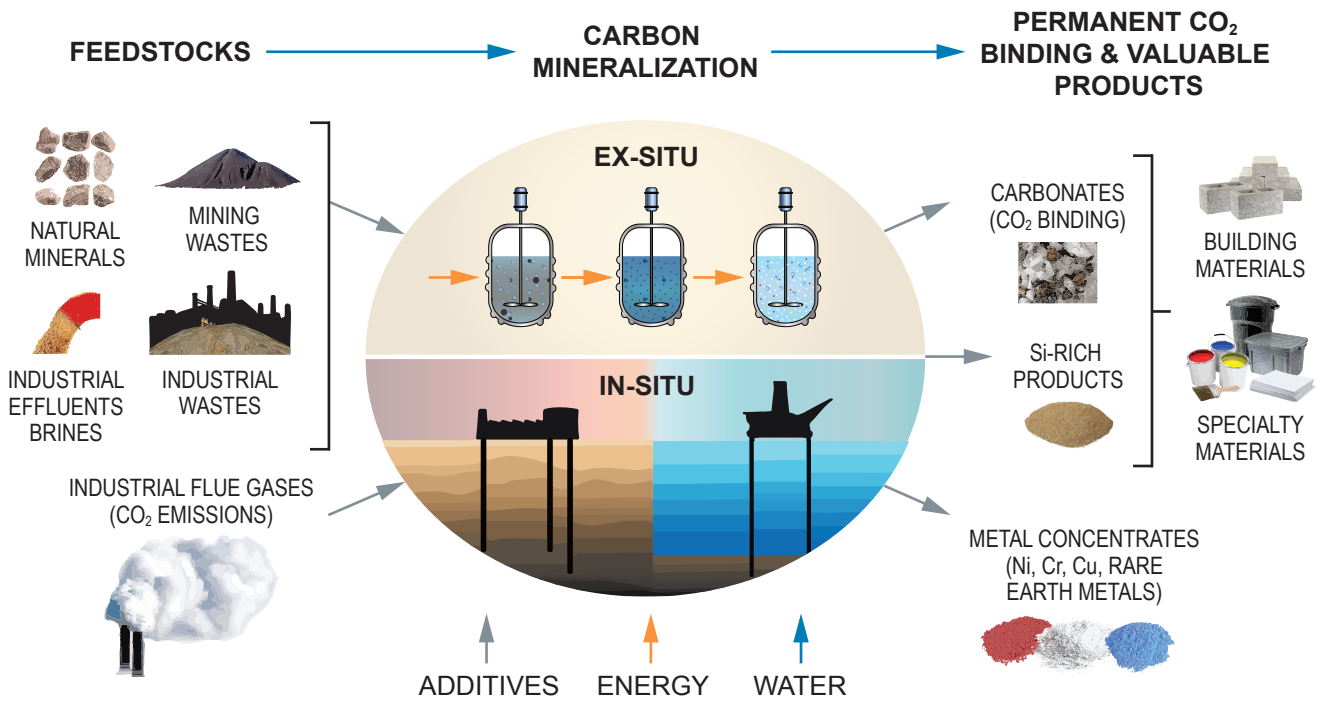
22 Gadikota, G. (2014). *Geo-Chemo-Physical Studies of Carbon Mineralization for Natural and Engineered Carbon Storage*, PhD diss., Columbia University.

23 Gadikota, G., Fricker, K., Jang, S-H., and Park, A-H. A. (2015). "Carbonation of Silicate Minerals and Industrial Wastes and Their Potential Use as Sustainable Construction Materials," *Advances in CO<sub>2</sub> Capture, Sequestration, and Conversion*, 1194:12–295. ACS Symposium Series. American Chemical Society. <https://doi.org/doi:10.1021/bk-2015-1194.ch012>.

24 Gerdemann, S. J., O'Connor, W. K., Dahlin, D. C., Penner, L. R., and Rush, H. (2007). "Ex Situ Aqueous Mineral Carbonation." *Environmental Science and Technology* 41 (7):2587–95. <https://doi.org/10.1021/es0619253>.

25 Bodénan, F., Bourgeois, F., Petiot, C., Augé, T., Bonfils, B., Julcour-Lebigue, C., Guyot, F., et al. (2014). "Ex Situ Mineral Carbonation for CO<sub>2</sub> mitigation: Evaluation of Mining Waste Resources, Aqueous Carbonation Processability and Life Cycle Assessment (Carmex Project)." *Minerals Engineering*. <https://doi.org/10.1016/j.mineng.2014.01.011>.

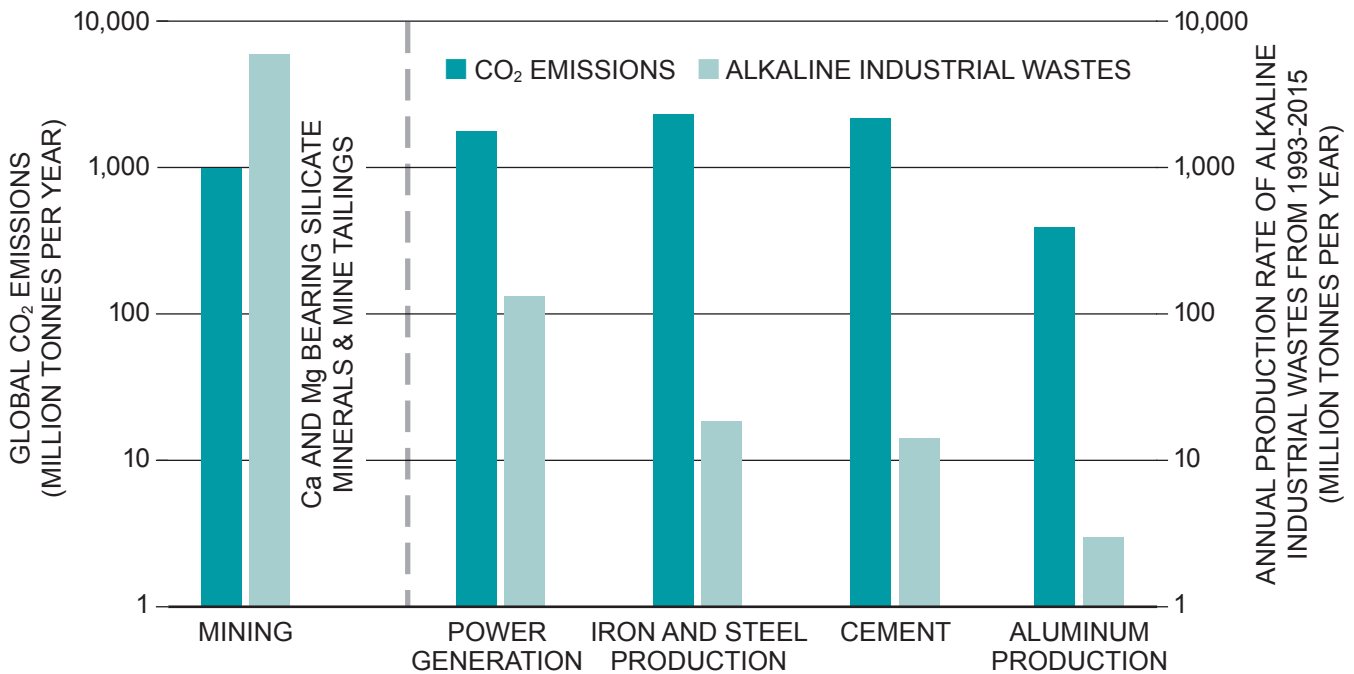
26 U.S. Department of Energy, Office of Fossil Energy. (2018). "Accelerating Breakthrough Innovation in Carbon Capture, Use, and Storage," Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, September 2017, Houston.



Source: U.S. Department of Energy, Office of Fossil Energy, *Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage*, Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop, 2017.

Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique; Au-Hung Park and Xiaozhou Sean Zhou, Columbia University.

**Figure 9-7. Scheme of Carbon Mineralization and Range of its Products**



Sources: Sources: Gadikota, G., Fricker, K., Jang, S-H., and Park, A-H.A. "Carbonation of Silicate Minerals and Industrial Wastes and Their Potential Use as Sustainable Construction Materials," in *Advances in CO<sub>2</sub> Capture, Sequestration, and Conversion*, 1194:12–295, ACS Symposium Series, American Chemical Society, 2015; and Bodénan, F., Bourgeois, F., Petiot, C., Augé, T., Bonfils, B., Julcour-Lebigue, C., Guyot, F., et al., "Ex Situ Mineral Carbonation for CO<sub>2</sub> mitigation: Evaluation of Mining Waste Resources, Aqueous Carbonation Processability and Life Cycle Assessment (Carmex Project)," *Minerals Engineering*, May 2014.

**Figure 9-8. U.S. Annual Emission Rate of CO<sub>2</sub> Produced by Industrial Sector and Corresponding Co-Generated Alkaline Industrial Wastes**

of research on these topics has formed in recent years, which has been primarily reported at international conferences on Accelerated Carbonation for Environmental and Materials Engineering, held in London (2006), Rome (2008), Turku (2010), Leuven (2013), New York City (2015), and Newcastle (2018). With this context, the following sections focus on the different pathways available for the accelerated conversion of CO<sub>2</sub> to calcium and magnesium carbonates.

## 1. Technology to Market Experience

The efforts in commercializing the conversion of CO<sub>2</sub> to carbonates can be broadly classified into four categories. The first category involves converting CO<sub>2</sub> to carbonate-bearing chemicals such as sodium bicarbonate. This approach is being commercialized by Carbon Free Chemicals. The second is geared toward using CO<sub>2</sub> for curing building materials as proposed by Solidia Technologies and CarbonCure. A third category involves converting CO<sub>2</sub> to carbonates using waste residues (fly ash, steel slag) for integration into building materials, which is being scaled up by Carbon8, GreenOre, Mineral Carbonation International, and Carbstone Innovation. Fourth, Carbon Upcycling Technologies is reacting waste CO<sub>2</sub> with solid feedstock (fly ash, petcoke, graphite) to create stable, high-strength solid nanoparticles.

One of the key advantages of commercializing technologies associated with CO<sub>2</sub> conversion to carbonates is the additional environmental benefits that accrue beyond the CO<sub>2</sub> used and converted to carbonates. The CO<sub>2</sub> curing approach utilized by Solidia Technologies eliminates at least 1.5 gigatonnes of CO<sub>2</sub>, reduces the use of fresh water reserves by 3 trillion tons, reduces energy consumption by 260 million barrels of oil, and eliminates 100 million tonnes of concrete landfill waste.<sup>27</sup> Using a patented process known as hydrothermal liquid phase sintering, cementitious materials are prepared at temperatures much lower than conventional sintering temperatures.<sup>28</sup> Further, CO<sub>2</sub> loaded with MEA can be

directly reacted with calcium silicate to produce calcium carbonate.<sup>29</sup>

Another company, CarbonCure, is injecting CO<sub>2</sub> directly into concrete to not only sequester it but to increase concrete performance and reduce the amount of cement—a high CO<sub>2</sub> footprint component—needed in the concrete mixture. Start-ups such as GreenOre and Mineral Carbonation International are converting steel slag produced by Baotao Steel in China to carbonated materials. Both direct and indirect approaches of converting CO<sub>2</sub> to carbonates starting with steel slag as the precursor material were evaluated. Further, the carbonate-bearing materials are being evaluated for their potential use as construction materials. These commercial activities illustrate the success in translating innovations in converting CO<sub>2</sub> to carbonates into the marketplace.

Most industrial developments involve production of calcium carbonates even though Mg is far more abundant. The potential for developing mineralization technologies that produce Mg-based construction materials is significant. This potential remains to be harvested. There are currently numerous public domain patents about magnesia-based hydraulic binders, dating as far as 1889.<sup>30</sup> It remains to be seen whether Mg-based mineralization products can be utilized to produce commercially and normatively acceptable binders for the construction sector, whether structural or nonstructural. Using Mg-based mineralization products to produce road infrastructure is also worth pursuing.

## 2. Product Options

For mineral carbonation to become economically feasible, the valorization of the resulting material could help reduce the overall cost of the process. This section outlines some recent developments with this objective, mainly to produce construction materials that either contain carbonated products or are formed by means of carbonation.

27 Solidia corporate website. <http://solidiatech.com/>.

28 Riman, R. E., and Atakan, V. (2012). "Systems and Methods for Carbon Capture and Sequestration and Compositions Derived Therefrom." Google Patents.

29 Li, Q., Gupta, S., Tang, L., Quinn, S., Atakan, V., and Riman, R. E. (2016). "A Novel Strategy for Carbon Capture and Sequestration by RHLPD Processing." *Frontiers in Energy Research*. <https://doi.org/10.3389/fenrg.2015.00053>.

30 Cummings, U. Cement. Patent 402,511. 1889, issued 1889.



Calcium carbonate is a mineral with several applications, and it is indispensable in the industries of paper, paint, and plastic where it is used as a filler or pigment. Calcium carbonate is also used as filler or coating pigment in rubbers and adhesives; as extender and pH buffer in paints; as filler and color stabilizer in concrete; for environmental pollution control and remediation in flue gas and water treatment; in fertilizers and animal feed as calcium supply; and in the production of glass, ceramics, cosmetics, and hygienic products. Due to the strict quality requirements for other industrial uses, however, it is preferable to synthesize calcium carbonate under controlled conditions as precipitated calcium carbonate (PCC). This product has the same chemical composition as any other naturally occurring calcium carbonate (chalk, limestone, marble), except it is produced artificially under conditions that result in a high-quality product with specific characteristics.

High-purity limestone (97% to 98%) in  $\text{CaCO}_3$  is typically used as the calcium source for the production of PCC. One recent research trend, however, is the use of alternative sources of calcium for PCC synthesis. One team of researchers has reported on using dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] as the starting material,<sup>31</sup> while another team has developed an indirect aqueous carbonation process for producing high-grade PCC (>99 weight%  $\text{CaCO}_3$ ) starting from waste gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).<sup>32</sup>

Calcium carbonate that is industrially used as a filler or pigment is most commonly calcite due to its stability and easy production routes. Aragonite, however, presents some improved physical and mechanical properties. Polyvinyl alcohol or polypropylene composites with aragonite filler show improved tensile strength, impact strength, glass temperature, and decomposi-

tion temperature,<sup>33</sup> while aragonite-containing paper coating benefits from improved brightness, opacity, strength, and printability.<sup>34</sup>

Several researchers have shown that finely milled basic oxygen furnace (BOF) slag, a waste product from the steel industry, can be used as a cement replacement in mortars and concretes.<sup>35,36,37,38</sup> Others have combined BOF slag with blast furnace slag<sup>39</sup> where it acts as a basic activator due to its free lime content. However, because the use of BOF slag as a binder requires intense grinding and given its high metallic iron content, this processing step requires a high-energy demand that incurs high cost. Carbon mitigation would come in the form of using the slag as a binder rather than a more carbon-intensive product such as Portland cement.

However, aggregates can also be an attractive product outlet for carbonated minerals. One research team calculated the  $\text{CO}_2$  sequestration capacity through mineral carbonation of alkaline industrial wastes that can be subsequently used as aggregates in the construction domain at 7.6 Mt  $\text{CO}_2$ /year for the United States.<sup>40</sup> Out of that quantity, 0.6 Mt  $\text{CO}_2$ /year represents the amount of emissions avoided by reducing the

31 Mantilaka, M.M.M.G.P.G, Karunaratne, D.G.G.P, Rajapakse, R.M.G., and Pitawala, H.M.T.G.A. (2013). "Precipitated Calcium Carbonate/Poly (Methyl Methacrylate) Nanocomposite Using Dolomite: Synthesis, Characterization and Properties." *Powder Technology* 235. Elsevier:628–32.

32 de Beer, M., Doucet, F. J., Maree, J. P., and Liebenberg, L. (2015). "Synthesis of High-Purity Precipitated Calcium Carbonate during the Process of Recovery of Elemental Sulphur from Gypsum Waste." *Waste Management*. <https://doi.org/10.1016/j.wasman.2015.08.023>.

33 Hu, Z., Shao, M., Cai, Q., Ding, S., Zhong, C., Wei, X., and Deng, Y. (2009). "Synthesis of Needle-like Aragonite from Limestone in the Presence of Magnesium Chloride." *Journal of Materials Processing Technology*. <https://doi.org/10.1016/j.jmatprotec.2008.04.008>.

34 Ota, Y., Inui, S., Iwashita, T., Kasuga, T., and Abe, Y. (1995). "Preparation of Aragonite Whiskers." *Journal of the American Ceramic Society* 78 (7). Wiley Online Library:1983–84.

35 Mahieux, P. Y., Aubert, J. E., and Escadeillas, G. (2009). "Use of Weathered Basic Oxygen Furnace Slag in the Production of Hydraulic Road Binders." *Construction and Building Materials*. <https://doi.org/10.1016/j.conbuildmat.2008.02.015>.

36 Wang, Q., Yan, P., Yang, J., and Zhang, B. (2013). "Influence of Steel Slag on Mechanical Properties and Durability of Concrete." *Construction and Building Materials* 47. Elsevier:1414–20.

37 Belhadj, E., Diliberto, C., and Lecomte, A. (2012). "Characterization and Activation of Basic Oxygen Furnace Slag." *Cement and Concrete Composites*. <https://doi.org/10.1016/j.cemconcomp.2011.08.012>.

38 2014. "Properties of Hydraulic Paste of Basic Oxygen Furnace Slag." *Cement and Concrete Composites*. <https://doi.org/10.1016/j.cemconcomp.2013.09.016>.

39 Guo, X., and Shi, H. (2013). "Modification of Steel Slag Powder by Mineral Admixture and Chemical Activators to Utilize in Cement-Based Materials." *Materials and Structures/Materiaux et Constructions*. <https://doi.org/10.1617/s11527-012-9970-7>.

40 Kirchofer, A., Becker, A., Brandt, A., and Wilcox, J. (2013). "CO<sub>2</sub> Mitigation Potential of Mineral Carbonation with Industrial Alkalinity Sources in the United States." *Environmental Science and Technology*. <https://doi.org/10.1021/es4003982>.



exploitation of natural sand, gravel, granite, and limestone. Besides capture of CO<sub>2</sub>, which is desirable for emissions reduction, mineral carbonation has also been reported to yield positive effects in terms of basicity and the leaching behavior of alkaline earth metals, heavy metals, and metalloids from steelmaking slags.<sup>41</sup>

Beyond construction materials, which is the largest volume outlet for carbonated minerals, one research team has identified a second product outlet for carbonation within oil-shale power plants by utilizing the C-a<sub>2</sub><sup>+</sup>-saturated alkaline water (pH 12–13) that is recycled between the plant and sedimentation ponds for transport of the ash to wet, open-air deposits.<sup>42</sup> The goal is to intensify the water neutralization process and use the wastewater as a calcium source for the production of PCC. The PCC formed is characterized by a regular rhombohedral structure and a homogeneous particle size (~5 μm) distribution. It has also been discovered that to avoid agglomeration of the particles and redissolution of CaCO<sub>3</sub>, the neutralization process must be divided into two stages: PCC precipitation and separation at high pH values in the first stage, followed by decreasing the residual alkalinity of the wastewater to acceptable disposal levels (pH ~8–8.5) in the second stage.

## D. Biological CO<sub>2</sub> Use

Biological CO<sub>2</sub> use refers to the conversion of CO<sub>2</sub> to biomass, chemicals, and fuels via biological pathways. Photosynthetic CO<sub>2</sub> conversion mimics natural plant growth that occurs in sunlight. Photosynthesis can use natural and artificial light to grow algae and cyanobacteria to produce bioenergy.

There are several unique nonphotosynthetic pathways being considered as well. For non-photosynthetic conversion, the required energy comes from reduced inorganic compounds or the

waste gases from industrial sources (spent syngas from steel plants) instead of the sun. Microorganisms can produce biofuels (ethanol) in dark conditions by using the energy in waste gases (CO, CH<sub>4</sub>, H<sub>2</sub>). In recent years, hybrid schemes combining chemical conversion of CO<sub>2</sub> to C<sub>1</sub> compounds (formate, CO), and the biological conversion of C<sub>1</sub> compounds into C<sub>2</sub><sup>+</sup> compounds, are being developed to synergistically enhance the overall conversion process and improve selectivity toward a target product.

Microorganisms can capture and convert CO<sub>2</sub> into chemicals, chemical intermediate, or fuels through either photosynthetic or nonphotosynthetic processes. Pathways include the direct conversion of CO<sub>2</sub> using sunlight and photosynthetic microorganisms, artificial light and microorganisms, and hybrid approaches that use electricity to help generate components for CO<sub>2</sub> that can be converted utilizing biological pathways. Photosynthetic microorganisms such as green algae or cyanobacteria have been used as found in nature or modified using genetic manipulation tools to convert CO<sub>2</sub> into precursors for the generation of fuels and chemicals, dietary proteins and as directed generation of compounds such as ethanol, butanol, 2,3-butanediol, 1,3-propanediol, ethylene, isoprene, squalene, and farnesene.

*Photosynthetic Processes.* Initially there was a strong economic case for developing algal-based biofuels to either augment or replace petroleum-based fuels. More recently, the case has been less clear because algae cultivation has presented significant challenges, including inefficient capture of total solar radiation energy (3% to 6%), limitations of algae to effectively convert CO<sub>2</sub>, and the cost and development of infrastructure for physically processing the algae (dewatering and extraction). To compensate for the low efficiencies, cultivation ponds or bioreactors are often designed to maximize light exposure through large volume and surface area, which makes algal cultivation land and water intensive. Multiple reports describe the state of the science and research challenges for algal biofuels.<sup>43</sup>

41 Bodor, M., Santos, R. M., Kriskova L., Elsen, J., Vlad, M., and Van Gerven, Tom. (2013). "Susceptibility of Mineral Phases of Steel Slags towards Carbonation: Mineralogical, Morphological and Chemical Assessment." *European Journal of Mineralogy*. <https://doi.org/10.1127/0935-1221/2013/0025-2300>.

42 Uibu, M., Velts, O., and Kuusik, R. (2010). "Developments in CO<sub>2</sub> Mineral Carbonation of Oil Shale Ash." *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2009.09.058>.

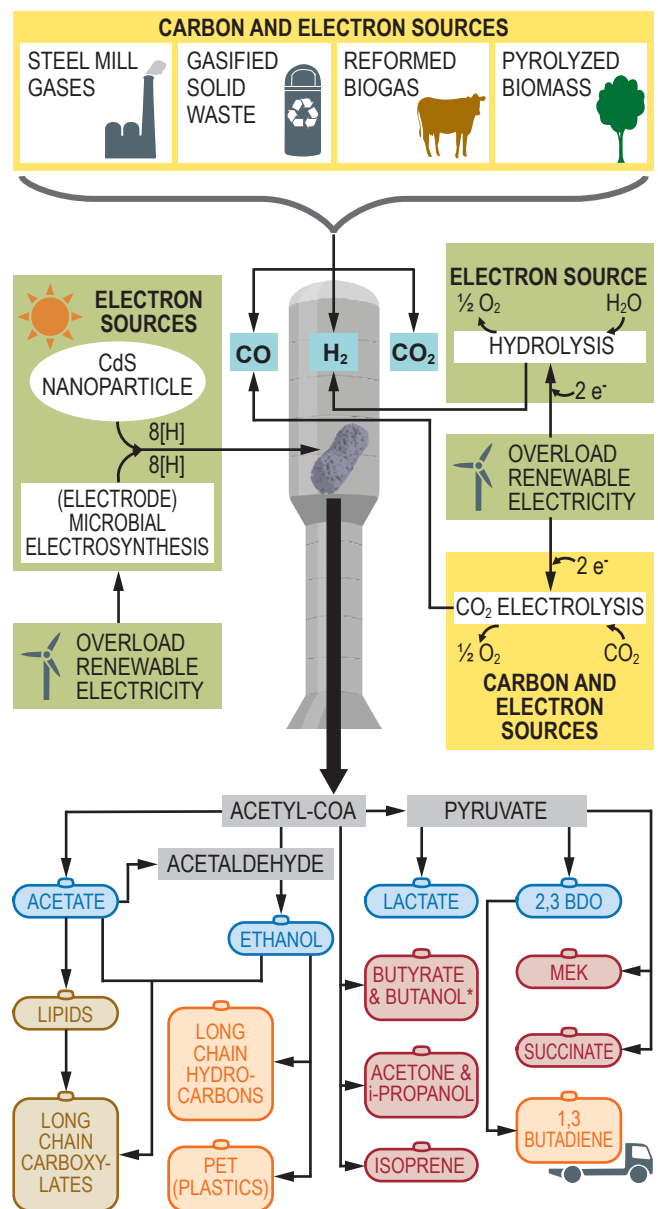
43 U.S. Department of Energy, Bioenergy Technologies Office. (2017). "Rewiring Carbon Reduction." [https://biomassboard.gov/pdfs/tac\\_2017\\_q3\\_rowe.pdf](https://biomassboard.gov/pdfs/tac_2017_q3_rowe.pdf).

**Nonphotosynthetic Processes.** Light-independent CO<sub>2</sub> fixation may occur within nonphotosynthetic biological processes that use chemolithotrophic microorganisms. Chemolithotrophs derive their energy from the oxidation of reduced inorganic compounds (molecular hydrogen, carbon monoxide, sulfides) and their carbon from CO<sub>2</sub>. Several companies (Lanzatech, Coskata, INEOS) have attempted to use a class of chemolithotrophs (acetogens) to convert CO<sub>2</sub> to fuels and chemicals via gas fermentation.

Gas fermentation using chemolithotrophic microorganisms known as acetogens has been demonstrated using CO, H<sub>2</sub>, and CO<sub>2</sub> gas mixtures as a feedstock. Certain acetogens can produce reduced products such as ethanol and 2,3-butanediol. Acetogens possess a biological water-gas shift capability that enables them to reversibly undertake the conversion of CO and H<sub>2</sub>O to H<sub>2</sub> and CO<sub>2</sub>. This bioreaction enables these organisms to operate across a broad array of gas compositions to produce reduced products such as ethanol. It also enables processes that use these organisms to tolerate rapid fluctuations in the composition of feed gas streams, removing the need for stable or fixed gas ratios while still producing valuable products with high selectivity.

Figure 9-9 is an overview of proposed feedstocks and the products generated using gas fermentation. In the figure, feedstocks to the gas fermentation platform are highlighted in yellow (carbon and electron sources) and green (electron sources). The feedstocks shown are at various stages of commercial deployment. Synthesis of all the products shown in the figure has been demonstrated, including (1) native products (blue text), (2) synthetic products produced through genetic modification (red text), (3) products generated through secondary fermentation of co-mixed cultures (brown text), and (4) products achieved through additional catalytic upgrading (orange text).

**Microbial Electrosynthesis.** An alternative non-photosynthetic route for biological use of CO<sub>2</sub> is providing reducing equivalents directly to a microorganism from electricity. This microbial electrosynthesis (MES) process has shown promise for using electrical current to reduce CO<sub>2</sub> to



- = NATIVE PRODUCT
- = ENGINEERED PATHWAY
- = SECONDARY OR CO/MIXED FERMENTATION
- = CATALYTIC UPGRADING

**ACRONYMS:**

- 2,3-BDO = 2,3-BUTANEDIOL
- CdS = CADMIUM SULFIDE
- MEK = METHYL ETHYL KETONE

\* Butyrate and butanol are both native and engineered products, depending on organism.

Source: Liew, F., Martin, M.E., Tappel, R.C., Heijstra, B.D., Mihalcea, C., Kopke, M., "Gas Fermentation – A Flexible Platform for Commercial Scale Production of Low-Carbon-Fuels and Chemicals from Was and Renewable Feedstocks," *Frontiers in Microbiology*, 7, (2016), p.1.

**Figure 9-9.** Overview of Feedstocks and Product Options for Gas Fermentation

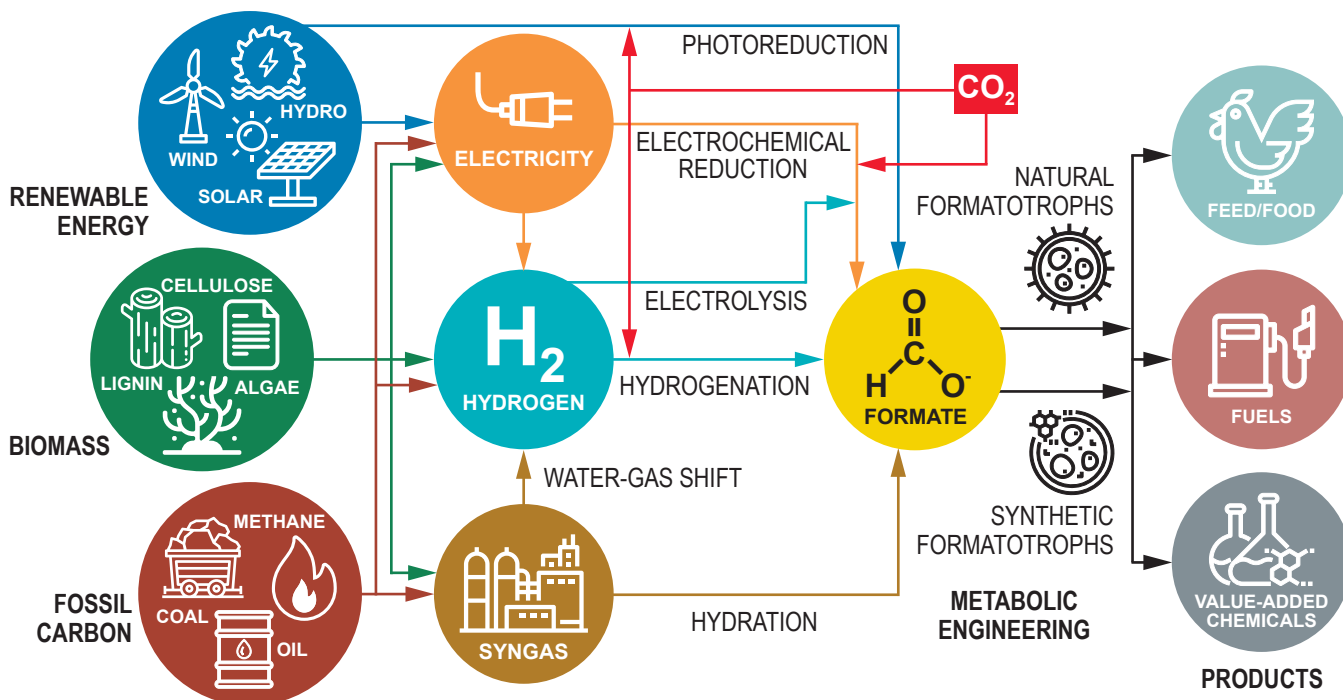
multicarbon products. MES can be an efficient process with 85% electron recovery, but challenges remain due to cultivation and maintenance of a dense biofilm on the cathode, electron transfer to this biofilm, and scale up of the overall system.

*Hybrid Approaches.* Gas fermentation of CO<sub>2</sub> to products is being scaled and commercialized, and it would be an ideal technology to combine with an electrochemical or chemical process that converts CO<sub>2</sub> to CO. Hybrid approaches combining electrochemical and biological processes are also being proposed where electrochemistry is used to reduce water and CO<sub>2</sub> into reactive intermediates such as H<sub>2</sub>, CO, and formate that can be used as feedstocks to biological processes. To date, electrochemistry has been effective for a two-electron transfer reaction such as the generation of H<sub>2</sub> via water splitting, reduction of CO<sub>2</sub> to CO, and the reduction of CO<sub>2</sub> to formate. However, electrochemistry has not yet been effective at converting CO<sub>2</sub> and water to more complex molecules required for today's fuels or chemicals. Biological routes are not as efficient at the conversion of

water and CO<sub>2</sub>, but can convert compounds such as H<sub>2</sub>, CO, and formate into fuels, chemicals, and nutrients.

With low-cost renewable electricity becoming a reality, such a hybrid approach could provide a cost-competitive route to generate a broad variety of fuels, chemicals, and nutrients using CO<sub>2</sub> as a carbon feedstock. Figure 9-10 shows a hybrid approach proposed by the Bar-Even group that combines the generation of a formate intermediate followed by biological upgrading of the formate to fuels or chemicals.<sup>44</sup> As Bar-Even explains the formate bio-economy concept, multiple approaches could support the synthesis of formic acid and formate from available sources. Formate could be then consumed by natural formatotrophic microbes or microbes engineered to efficiently assimilate formate to produce fuels, value-added chemicals, and protein meal for animal or human consumption.

<sup>44</sup> Yishai, O., Lindner, S. N., Gonzalez de la Cruz, J., Tenneboim, H., and Bar-Even, A., "The formate bio-economy," *Current Opinion in Chemical Biology*, 35, 2016, p1.



Source: Yishai, O., Lindner, S.N., Gonzalez de la Cruz, J., Tenneboim, H., and Bar-Even, A., "The formate bio-economy," *Current Opinion in Chemical Biology*, 35, (2016) p1.

**Figure 9-10.** Schematic Representation of the Formate Bio-Economy Concept

## 1. Technology to Market Experience

Several examples exist where companies are progressing precommercial and early commercial applications of biological conversion of CO<sub>2</sub>.

Qualitas Health is using green algae within open pond systems to generate nutrients such as omega-3, a high-value nutraceutical product. Algenol is using green algae within a photobioreactor system based on bags to generate similar products. In addition to using natural sunlight as an energy source, artificial light photobioreactor systems that generate a specific wavelength of light using highly efficient LED light systems are also being investigated. These artificial light systems would become cost-effective as more low-cost electricity becomes available with the deployment of more renewable electricity generation resources—wind, solar, and emissions-free fossil power plants with CO<sub>2</sub> capture and geological storage. Pond Technologies is demonstrating that these artificial light photobioreactor systems can convert CO<sub>2</sub> from a cement plant to generate fish food.

LanzaTech has commercialized a gas fermentation approach. Their first commercial facility produces 46,000 tonnes of ethanol from a waste gas produced from a steel mill in China. This approach offers a path to convert waste streams from industry, society (municipal solid waste), and agriculture into fuel and chemical products.

There have been large investments in algal biofuels technologies by start-ups such as Algenol, Cellana, and Sapphire as well as established companies such as ExxonMobil and Shell. While these companies initially focused on the generation of biofuels when crude oil prices were \$100/barrel, numerous start-up companies either did not survive or pivoted to the generation of higher valued products such as protein and food supplement (omega-3) when the price of oil decreased to less than \$40/barrel.

What follows is a list of companies and the type of biological conversion process they are pursuing along with brief assessments of the successes and challenges of each.

### a. *Photosynthetic Processes*

ExxonMobil has partnered with Synthetic Genomics to develop algae capable of generating high yields of oil from CO<sub>2</sub>, water, and sunlight. This partnership also announced that they are moving from the research and development (R&D) phase to the engineering phase and will begin conducting open pond studies in the next few years.

Qualitas Health is currently operating two algae farms using open pond technologies. At the Imperial Farm in Texas there are 45 acres of cultivation area and another 98 acres at the Columbus, New Mexico, site. Qualitas Health is also marketing two products: omega-3 and AlmegaPL (a high-quality EPA-rich omega-3).

Algenol has photobioreactor technologies that use bags, sunlight, and stack gases. Algenol is using this technology to generate blue-green algae that is capable of generating a range of all-natural products.

Pond Technologies uses an artificial light photobioreactor to grow algae from CO<sub>2</sub> that is used to produce fish food and algae-based superfoods, like spirulina and chlorella, that provide nutritious, vegan supplements for human consumption. Pond has a 20,000-liter demonstration unit that uses off-gas from a cement plant.

Global Microalgae and Cellana employ flue gas as their source of CO<sub>2</sub> and the U.S. Department of Energy is funding two projects using coal-derived flue gas. For one project, the University of Kentucky is Partnering with Duke Energy, and at the other, MicroBio Engineering is partnering with Orlando PUC.

Sapphire Energy developed open pond algae technology for the generation of oils for fuel production. The company built and operated the world's first commercial demonstration algae-to-energy facility near Columbus, New Mexico. Several demonstrations were conducted using oil generated from Sapphire technology, including test flights conducted by Continental Airlines and Japan Airlines. Between 2008 and 2012, the company raised more than \$244 million in funding from investors and received \$104.5 million via



government grants and loan guarantees. However, by 2017, with crude oil prices at around \$50/barrel—half the price of the late 2010s—Sapphire Energy ceased to exist. In 2017, it was bought by a farmer for pennies on the dollar.

Joule Unlimited developed genetically engineered cyanobacteria to produce diesel fuel or gasoline with only sunlight, water, and carbon dioxide. After raising more than \$200 million in funding in 2007, plans for a commercial plant near Hobbs, New Mexico, were scrapped and the company was shut down in 2017 due to the decline in oil prices.

### **b. Nonphotosynthetic Processes (Gas Fermentation)**

LanzaTech has commercialized a gas fermentation technology for the generation of ethanol and butanediol from CO-rich streams (steel mill off-gases) using a proprietary microbe in the family of acetogens (a gas-fermenting organism). LanzaTech has taken advantage of stack gases rich in CO, such as those from steel production, to develop and commercialize their gas fermentation technology beginning with ethanol as their first production plants to convert emissions from these processes to fuels and chemicals. Other facilities that use solid waste streams from agriculture and municipal waste employ gasification to produce a syngas that can be converted by gas fermentation to fuels and chemicals are also in development. LanzaTech has developed a specialized flow-through reactor system that effectively contacts the CO rich off-gas with their microbes.

LanzaTech has successfully started its first plant in China with a stated capacity of 46,000 tonnes of ethanol and has commercial units under construction in Europe, India, South Africa, and the United States. The company has developed a comprehensive genetic engineering capability for its gas fermenting microbial chassis. This has enabled the modification of its proprietary organism to facilitate the production of chemical products from the gas streams that it can access. LanzaTech has also demonstrated and certified a technology to further upgrade ethanol to jet fuel using a catalytic process technology.

Use of combined gases streams ( $H_2$  and  $CO_2$ ) has been demonstrated in the lab for gas fermenta-

tion by NovoNutrients, which produces a high-protein aquafeed product.

INEOS Bio built and operated an 8-million-gallon-per-year semi-commercial facility as a joint venture with New Planet Energy Holdings, LLC. This facility used a gas fermentation technology to convert municipal solid waste and cellulosic feedstocks into ethanol. The facility was also capable of producing up to 6 MW of electricity. The facility was commissioned in 2012 and INEOS claimed production of ethanol in 2013. In 2014, the company announced a major turnaround as it was discovered that little to no ethanol was produced due to the production of low levels of hydrogen cyanide. The installation of wet scrubbers to remove the hydrogen cyanide was expected to solve this problem. In 2016, INEOS announced it was selling its ethanol business because the market for ethanol had changed and the economic drivers for its technology were no longer aligned with its strategic objectives. The Vero Beach facility was sold in early 2018 to a consortium led by Texas-based Frankens Energy.<sup>45</sup>

Coskata was incorporated in 2006 to develop a gas fermentation technology to generate ethanol from gas generated via the gasification of wood chips. The company operated a semi-commercial pilot plant in Madison, Pennsylvania, but in 2015, the company went out of business. Coskata's technology formed the basis of a new company, Synata Bio, but the technology has not been scaled further.

### **c. Microbial Electrosynthesis**

Currently, microbial electrosynthesis research and development is found primarily in either academic or government laboratories.

### **d. Hybrid Approaches**

Hybrid approaches that combine the concept of using electrochemical techniques to generate reactive intermediates from  $CO_2$  followed by the biological conversion of the generated reactive

45 Voegele, E. (2018). "Former INEOS Bio site purchased for conversion into eco-district," *Biomass*, <http://biomassmagazine.com/articles/15089/former-ineos-bio-site-purchased-for-conversion-into-eco-district>.

intermediates to valued-added projects has been the subject of research conducted by academia and government labs. The nearest term commercial approach would be the electrochemical conversion of CO<sub>2</sub> to CO followed by conversion using gas fermentation technology such as the technology being commercialized by LanzaTech.

### e. Energy Extraction Technologies

Several efforts using CO<sub>2</sub> as a solvent in various extraction or synthesis processes have been launched. Examples include using supercritical CO<sub>2</sub> for botanical and plant oil extraction by Apeks Supercritical and Natac, respectively. Further, using supercritical CO<sub>2</sub> as a solvent in the synthesis of metal-organic frameworks has been proposed by ACSYNAM. The production of graphitic carbon for use in lithium-ion batteries via the electrochemical separation of CO<sub>2</sub> was proposed by Saratoga Energy Research Partners, LLC. SuperCritical Technologies is working toward using supercritical CO<sub>2</sub> power cycles to simplify

Elemental (AFDW)	Wt. %
C	54.0
O	35.5
H	8.2
N	1.8
S	0.2
P	0.3
Components	Dry wt. %
Fermentable carbohydrates	47.8
FAME lipids as free fatty acids	26.0
Protein	13.2
Non-fermentable carbohydrates	3.2
Glycerol	3.0
Ash	2.4
Sterols	1.8
Cell mass	1.6
Non-fuel polar lipid impurities	1.0

Source: Argonne National Laboratory, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory, *2017 Algae Harmonization Study: Evaluating the Potential for Future Algal Biofuel Costs, Sustainability, and Resource Assessment from Harmonized Modeling*, August 2018.

**Table 9-2. Elemental and Component Compositions Based on High-Carbohydrate Scenedesmus Biomass**

power generation. In addition to resource extraction, using CO<sub>2</sub> in energy extraction is being evaluated. TerraCOH has been exploring the potential for using CO<sub>2</sub> as a working fluid—an alternative to water—in enhanced geothermal systems. These are just a few examples of current commercialization efforts related to using CO<sub>2</sub> for energy and resource recovery.

## 2. Product Options

An advantage of microalgae is their ability to produce a range of products with differing values, providing a stepwise path to market entry. Some of those products, such as astaxanthin, a nutraceutical, command prices near \$1 million per ton because their polyunsaturated fats and protein content have intermediate value as feed supplements.

Table 9-2 shows the composition of a genus of high-carbohydrate algae called *Scenedesmus*.<sup>46</sup> This analysis shows a fatty-acid-methyl-ester lipid content of 26% and fermentable carbohydrates of 47.8%. The extracted lipids from green algae may be processed to biodiesel through transesterification and esterification, which involves reacting the oils with short-chain alcohols. Alternatively, the algae oil may be hydrogenated with hydrogen in a catalytic reactor to generate renewable diesel. Renewable diesel may be further processed in a catalytic isomerization process to generate a renewable jet fuel. The fermentable carbohydrates can be extracted and used for fermentation of fuels such as ethanol, isobutanol, or the higher valued products such as succinic acid.

Green algae has an amino acid profile that compares favorably with common food protein and could be an attractive source of dietary protein as animal feed and for human consumption. Green algae is also an attractive source of polyunsaturated fatty acids (omega-3)—eicosapentaenoic acid and docosahexaenoic acid). Omega-3

<sup>46</sup> Argonne National Laboratory, National Renewable Energy Laboratory, and Pacific Northwest National Laboratory. *2017 Algae Harmonization Study: Evaluating the Potential for Future Algal Biofuel Costs, Sustainability, and Resource Assessment from Harmonized Modeling*. August 2018. Golden, CO: National Renewable Energy Laboratory. NREL/ TP-5100-70715, <https://www.nrel.gov/docs/fy18osti/70715.pdf>.

fatty acids have a place in the consumer market, currently dominated by fish oils, as nutraceutical products.

Table 9-3 shows a summary of commodity chemicals and fuels that can be generated from CO<sub>2</sub> using cyanobacteria. The fuels and fuel precursors that can be produced include ethanol, butanol, fatty acids, heptadecane, limonene, and bisabolene. Chemicals that can be produced include 2,3-butanediol, 1,3-propanediol, ethylene, glycogen, lactate, 3-hydroxypropionic acid, isoprene, squalene, and farnesene.

Phytonix Solar Chemicals in Black Mountain, North Carolina, uses genetically engineered cyanobacteria to produce longer chain alcohols, including 1-octanol, which are considered to be a biodiesel.

Bench-top scale experiments have shown that MES technologies can generate ethanol, acetic acid, and butyric acid at low levels while products generated from a hybrid approach with gas fermentation as the biological step would generate ethanol, 2,3-butanediol, isopropanol, as well as potentially generating higher valued chemicals.

#### IV. LIFE-CYCLE ANALYSIS

The importance of accurate and rigorous life-cycle analyses on CO<sub>2</sub> use cannot be overstated. There is considerable thermodynamic difficulty in capturing CO<sub>2</sub> and then converting this CO<sub>2</sub> into a saleable product via processes that require significant energy input. Given that the primary driver of CO<sub>2</sub> use is to reduce or eliminate net carbon emissions to the atmosphere, it is necessary to approach all carbon capture and use (CCU) applications with life-cycle analyses in mind to determine and quantify a realistic reduction in CO<sub>2</sub> emissions for a product or process.

Life-cycle analysis needs to address the direct and indirect impacts from CO<sub>2</sub> emissions. Direct impacts are those associated with the long-term sequestration of CO<sub>2</sub>, which is based on the assumption that the CO<sub>2</sub> will not be re-released to the atmosphere. CCU takes credit for the CO<sub>2</sub> that is permanently embedded in the product or process minus the CO<sub>2</sub> that is

emitted upstream (mining, transport, processing). Indirect impacts are those claimed due to the potential replacement of an existing product or value chain.

Compound	Reported Production
Ethanol (C <sub>2</sub> H <sub>5</sub> OH)	5.5 g/L
Isobutanol (C <sub>4</sub> H <sub>10</sub> O)	0.5 g/L
N-Butanol (C <sub>4</sub> H <sub>10</sub> O)	2 mg/L/h
Fatty acids	> 130 mg/L
Heptadecane (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>2</sub> )	4.2 mg/g dry cell weight
Limonene (C <sub>10</sub> H <sub>16</sub> )	1 mg/L/OD <sub>730</sub> /day 4mg/L 7mg/L
Bisabolene (C <sub>15</sub> H <sub>24</sub> )	0.6 mg/L
2,3-Butanediol (C <sub>4</sub> H <sub>10</sub> O <sub>2</sub> )	2.4 g/L (after 21 days); 3 g/L (after 10 days, photomixotrophic condition); 12.6 g/L (continuous lighting with glucose and CO <sub>2</sub> ); 5.7 g/L (23-hr light cycling)
1,3-Propanediol (C <sub>3</sub> H <sub>8</sub> O <sub>2</sub> )	0.3 g/L
Ethylene (C <sub>2</sub> H <sub>4</sub> )	2.5 mL/h/OD <sub>730</sub>
Glycogen ((C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub> )	3.5 g/L (after 7 days)
Lactate (C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	0.8 g/L (after 2 weeks) 1.4 g/L (after 10 days)
3-HB (C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> )	0.8 g/L (after 6 days)
Isoprene (C <sub>5</sub> H <sub>8</sub> )	1.3 g/L (after 21 days)
Squalene (C <sub>30</sub> H <sub>50</sub> )	50 mg/L
Farnesene (C <sub>15</sub> H <sub>24</sub> )	5 mg/L

Source: National Academies of Sciences, Engineering, and Medicine. (2019). *Gaseous Carbon Waste Streams Utilization: Status and Research Needs*. Washington, DC: The National Academies Press.

**Table 9-3.** Commodity Chemicals and Fuels That Are Currently Synthesized from CO<sub>2</sub> from Cyanobacteria and Their Reported Production

For products such as CO<sub>2</sub>-fuels or some chemicals (urea), the CO<sub>2</sub> storage time is very short, ranging from a few days to a few months. Short storage times have no impact on the atmospheric concentration of CO<sub>2</sub>, so life-cycle analyses of these types of products can realistically only claim credit for indirect impacts on emissions.<sup>47</sup>

For products like construction aggregates or oil from CO<sub>2</sub> enhanced oil recovery (EOR), life-cycle analyses account for direct and indirect impacts because the CO<sub>2</sub> is sequestered for longer period of times (from centuries to thousands of years) and the CO<sub>2</sub>-based product could also replace conventional fossil fuel value chains.<sup>48,49,50,51</sup>

For other products, like chemical intermediates or CO<sub>2</sub>-based polyurethanes or polyols, there is debate on what their CO<sub>2</sub> storage time is and its impact on net CO<sub>2</sub> emissions. Current life-cycle analyses of polyols in the literature consider the storage time to be too short to claim direct impacts, and thus only account for indirect impacts.<sup>52,53</sup> However, the lifetime of a plastic item varies from days to decades depending upon the item's application and end-of-life management practices—recycling, landfilling, incinerat-

ing. It is expected that the CO<sub>2</sub> storage time for some applications could be extended well beyond 50 years through recycling.

Thus, differences in the types of CCU products, expected market sizes, and how direct and indirect impacts are accounted for have resulted in a broad range of values for the potential of CCU as a net carbon emissions reduction option.<sup>54,55,56,57</sup> For these reasons, a life-cycle analysis effort similar to the National Energy Technology Laboratory's Bituminous Baseline Reports is suggested, which provides transparent metrics and a standard analysis for determining the cost associated with carbon capture technologies deployed on a variety of fossil fuel power plants. While the reports do not cover every conceivable outcome and are a representation of a typical technology deployment, they are a useful and valuable tool in determining the various sensitivities of technologies and for making relative comparisons.

Finally, it is notable that CCU may have the opportunity to address safety and toxicity concerns associated with the current reagents used in conventional polymer production. Two teams of researchers indicated a decrease in scores for eutrophication, acidification, and toxicity, which are due to the replacement of propylene oxide by CO<sub>2</sub>.<sup>58,59</sup> Another team, however, indicates that CO<sub>2</sub>-based polymers have higher material intensity (raw material input and total material requirement) than fossil-based polymers and that balances between process safety and overall

47 National Academies of Sciences, Engineering, and Medicine. (2019). *Gaseous Carbon Waste Streams Utilization: Status and Research Needs*. Washington, DC: The National Academies Press. <https://doi.org/10.17226/25232>.

48 Khoo, H. H., Sharratt, P. N., Bu, J., Yeo, T. Y., Borgna, A., Highfield, J. G., et al. "Carbon capture and mineralization in Singapore: preliminary environmental impacts and costs via LCA." *Industrial & Engineering Chemistry Research*. 2011;50(19):11350-7.

49 Kirchofer, A., Brandt, A., Krevor, S., Prigiobbe, V., and Wilcox, J. "Impact of alkalinity sources on the life-cycle energy efficiency of mineral carbonation technologies." *Energy & Environmental Science*. 2012;5(9):8631-41.

50 Cooney G., Littlefield, J., Marriott, J., and Skone, T. J. "Evaluating the climate benefits of CO<sub>2</sub>-enhanced oil recovery using life cycle analysis." *Environmental Science & Technology*. 2015;49(12):7491-500.

51 Nuñez-López, V., Gil-Egui, R., Gonzalez-Nicolas, A., and Hovorka, S. "Carbon balance of CO<sub>2</sub>-EOR for NCNO classification." *Energy Procedia*. 2017;114:6597-603.

52 Von der Assen N., and Bardow, A. "Life cycle assessment of polyols for polyurethane production using CO<sub>2</sub> as feedstock: insights from an industrial case study." *Green Chemistry*. 2014;16(6):3272-80.

53 Fernández-Dacosta, C., Van Der Spek, M., Hung, C. R., Oregionni, G. D., Skagestad, R., Parihar, P., et al., "Prospective techno-economic and environmental assessment of carbon capture at a refinery and CO<sub>2</sub> utilisation in polyol synthesis." *Journal of CO<sub>2</sub> Utilization*. 2017;21:405-22.

54 Mac Dowell, N., Fennell, P. S., Shah, N., and Maitland, G. C. "The role of CO<sub>2</sub> capture and utilization in mitigating climate change." *Nature Climate Change*. 2017;7(4):243.

55 Abanades, J. C., Rubin, E. S., Mazzotti, M., and Herzog, H. J. "On the climate change mitigation potential of CO<sub>2</sub> conversion to fuels." *Energy & Environmental Science*. 2017;10(12):2491-9.

56 Aresta, M., Dibenedetto, A., and Angelini, A. "The changing paradigm in CO<sub>2</sub> Utilization." *Journal of CO<sub>2</sub> Utilization*. 2013;3:65-73.

57 Global CO<sub>2</sub> Initiative. (2016). *Global Roadmap for Implementing CO<sub>2</sub> Utilization*. doi: 10.3998/2027.42/146529, <http://hdl.handle.net/2027.42.146529>.

58 Von der Assen, N., and Bardow, A. "Life cycle assessment of polyols for polyurethane production using CO<sub>2</sub> as feedstock: insights from an industrial case study." *Green Chemistry*. 2014;16(6):3272-80.

59 Fernández-Dacosta, C., Van Der Spek, M., Hung, C. R., Oregionni, G. D., Skagestad, R., Parihar, P., et al., "Prospective techno-economic and environmental assessment of carbon capture at a refinery and CO<sub>2</sub> utilisation in polyol synthesis." *Journal of CO<sub>2</sub> Utilization*. 2017;21:405-22.



resource consumption may also be of interest for life-cycle analyses.

## V. RESEARCH AND DEVELOPMENT NEEDS

It will take many technologies to address the wide range of CO<sub>2</sub> use pathways, and they will require support to meet the stringent requirements of transitioning from basic research to commercialization. As mentioned earlier in the chapter, the deployment of these technologies will depend on the availability of affordable renewable energy and green (water splitting) and blue (fossil-based) hydrogen sources. Thus, it is difficult to estimate the timing of commercialization for each CO<sub>2</sub> use technology. The high-level R&D needs are listed in the following sections and are quite specific for each conversion pathway. Finally, a consolidated R&D funding support recommendation for CO<sub>2</sub> use is quantified at the end of this section.

### A. Thermochemical

Future study should continue to improve the selectivity, activity, and stability of the catalytic materials and include both theoretical and experimental characterization for fundamental understanding, which would help to identify mechanistic pathways. For catalysts that have proved to be active, selective, water-resistant, and cost-effective in the range of lower temperatures—such as from 373 K to 573 K where hydrogenation is more thermodynamically favored—long-term stability in catalytic performance should be examined as well as the solutions to prevent deactivation.

Other key challenges that need to be resolved for many CO<sub>2</sub> conversion reactions are improving selectivity to the desired products and catalyst stability with regard to by-products, such as water, and impurities in feedstocks. The latter is particularly important but is often not studied in detail when new catalysts are developed, especially in academic laboratories. Thus, joint efforts between academia and industry would be beneficial.

More laboratory research and computational study, as well as pilot-scale research and devel-

opment, are required for establishing efficient and practical processes for CO<sub>2</sub> use to promote sustainable development and to reduce rising CO<sub>2</sub> emissions. Meanwhile, investigations on developing more efficient and cost-effective ways to produce H<sub>2</sub> from water using renewable energy is also indispensable for CO<sub>2</sub> hydrogenation with environmental and economic viability in the near term.

### B. Electrochemical and Photochemical

The main research in this area includes the development of novel catalysts for better selectivity, activity, and stability; polymer membranes with high robustness and ionic conductivities; and novel cell or multicell stack design and manufacturing. The development of an effective cathode for CO<sub>2</sub> reduction is a major obstacle that has garnered much research attention. Although both homogeneous and heterogeneous catalysts for CO<sub>2</sub> electroreduction have been extensively studied, heterogeneous catalysts are more likely to be implemented in practical systems considering their robustness.

In the case of C<sub>1</sub> products, Faradaic efficiencies for CO and formic acid have been consistently high (>80%) with the majority of these catalysts being silver-based for CO production and tin-based for formic acid production. This is important because reduced Faradaic efficiencies require additional energy input to drive the reaction. If a low Faradaic reaction is coupled with a high carbon intensity energy source, then life-cycle CO<sub>2</sub> emissions will increase and intended carbon mitigation will not be achieved. Therefore, highly efficient pathways with low-carbon energy sources should be pursued. Alternative anodic reaction with better energetic efficiency should also be investigated.

The electrochemical and photochemical conversion pathways share similar challenges but also differ in terms of light harvesting, device design, etc. The scale up of catalysts, membrane systems, and cells would be another important R&D area.

The development of novel electrolytes that can provide high CO<sub>2</sub> solubility is also an important R&D area, and it has great potential to combine

CO<sub>2</sub> capture and conversion into a single process that improves overall efficiency. The development of hybrid systems combining electrochemical and photochemical systems with thermochemical and biochemical conversion pathways will be very important for transformative technological advancements.

### C. Carbonation and Cement

Carbonation has the largest potential for immediate CO<sub>2</sub> use and long-term sequestration. However, the barriers to entry are typically associated with colocating the CO<sub>2</sub> sources with the necessary mineral feedstocks. In addition, there could be resistance to adopting alternative building materials which would need to be addressed through product certification.

While the chemistry of carbon mineralization and concrete curing are relatively understood, these chemistries can be quickly complicated as the feedstock changes. Thus, deeper understanding of integrated reaction pathways, the use of chemical (ligands) and biological catalysts (carbonic anhydrase), and innovative separation of valuable products (carbonates) and by-products (metals and rare earth elements) are required for the future deployment of these technologies. The optimization of the overall reaction will also involve the advanced understanding of chemomorphological-mechanical coupling and, thus, both modeling and experimental studies should be carried out for various carbonation feedstocks. The characterization and performance testing of produced materials for various applications ranging from paper fillers to construction materials will also be important. At larger scales of R&D, the energy and materials integration for process intensification should be investigated to ensure the net CO<sub>2</sub> sequestration benefit.

### D. Biological

Biological conversion is slower than alternative CO<sub>2</sub> use pathways given the inherent kinetics of this technology. There are many pathways and corresponding TRL levels associated with biological CO<sub>2</sub> conversion, and progressing multiple approaches for moving biological conversion forward, in particularly for accelerating the kinetics,

is worthwhile. For technologies at a lower TRL, additional research must be complemented by additional mechanisms, such as renewable fuel standards or other fiscal incentives, to create a market for biological CO<sub>2</sub> conversion products. Algae technologies using natural sunlight should be developed to generate high valued but low-volume nutraceuticals. Artificial light biophotoreactors technologies that are currently being commercialized should be applied to the systems with renewable electricity combined with highly efficient LED light sources for generation of algae-derived nutraceuticals, proteins, and chemicals. In both cases, light efficiency, selectivity, and associated reactor systems for the production of higher volume and the lower cost of chemicals and fuels should be investigated. Gas fermentation also has several challenges, including effective mass transfer in the gas-to-liquid phase and product separation. These challenges should be studied in both lab- and pilot-scale projects.

As discussed earlier, hybrid systems have great potential to overcome R&D challenges in each pathway. It has been suggested that CO<sub>2</sub> to C<sub>1</sub> conversion is easier via a chemical pathway while C<sub>1</sub> to C<sub>2</sub><sup>+</sup> conversion would be easier via a biological pathway. Therefore, understanding how to combine different reactions into a single system or combined systems should be investigated in both fundamental and large-scale research projects. The integration of intermittent energy sources into a biological system would also be challenging because the time scale for biological conversion and the availability of renewable energy in a given time period may not match.

### E. Multilevel R&D Funding Structure

Considering these R&D challenges and needs, this study recommends \$500 million over 10 years for support of basic science. This is particularly important for CO<sub>2</sub> use technologies because many of them are still at a low TRL.

Fundamental research funding is very important to advance science and engineering related to these technological areas by providing enough government support. Funding for multiple principal investigator activities and center grants focused on scientific discoveries should be

created. Interdisciplinary research is very important for CO<sub>2</sub> technologies because they require expertise in a wide range of fundamental areas, including materials, catalysis, reaction engineering, and systems engineering. Collaborations between academia and industry should be encouraged via center grants. Previous versions of ARPA-E type funding for the acceleration of tech-to-market transitions can support academic researchers in working with industrial partners, and the New ARPA-E type funding can be awarded to start-up companies.

In addition, the study recommends a second tranche of \$500 million in funding over 10 years—for years 5 to 15—to support pilots, demonstration projects, and progression toward deployment by building on successes that emerge from the earlier, basic science funding phase. To progress this, it is recommended that projects are field deployed to at least the level of the National Carbon Capture Center, Wyoming Integrated Test Center, or a similar practical demonstration environment that uses real flue gas sources in an industrial environment.

## VI. CONCLUSIONS

CO<sub>2</sub> use offers an important set of tools for reducing carbon emissions while creating economic opportunities through the production of products that are necessary for industrialized society. Even though the near-term scale of potential reductions delivered by CO<sub>2</sub> use will be much smaller than can be achieved by CO<sub>2</sub> geologic storage (described in Chapter 7, “CO<sub>2</sub> Geologic Storage”) and CO<sub>2</sub> EOR (described in Chapter 8, “CO<sub>2</sub> Enhanced Oil Recovery”), there will be niche opportunities for CO<sub>2</sub> use to create value in markets by providing the necessary carbon-based or carbon-consuming products for advanced economies.

These opportunities should be pursued in parallel with geologic storage and EOR as a potential means to offset carbon mitigation costs while advancing the field so that CO<sub>2</sub> use may scale up in the coming decades. EOR and geologic storage are necessary and scalable in the near term, but for carbon emissions to continue to decrease, carbon-based products will eventually need to

be sourced from CO<sub>2</sub> rather than fossil fuel feedstocks—unless those feedstocks are low carbon from the application of CCUS. This will require a significant investment in RD&D, time, and increasing knowledge resources.

The four main types of CO<sub>2</sub> use technologies—thermochemical, electrochemical and photochemical, carbonation, and biological conversion—are all worthy of progression because not every pathway will be feasible in all regions. Many considerations, such as local environmental factors, markets, and access to affordable low-carbon energy sources will be present domestically and abroad in various ratios. For this reason, it is necessary to consider all approaches without prematurely defining winners because certain technologies may prove to be beneficial domestically while others may prove themselves in export markets.

Through continued investment, a nearly limitless array of products can potentially be brought to market via a number of CO<sub>2</sub> use pathways. The engineered use of CO<sub>2</sub> as a feedstock can impact a wide range of carbon-based products such as fuels, fertilizers, polymers, industrial chemicals, building materials such as carbonates and cements, carbon nanotubes, and other products that are critical to the global economy.

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