



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-739322

Carbon Dioxide Utilization (CO2U) ICEF Roadmap 2.0

D. Sandalow, R. Aines, J. Friedmann, C.
McCormick, S. McCoy

November 2017

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

CARBON DIOXIDE UTILIZATION (CO₂U) ICEF ROADMAP 2.0



November 2017

Preface

Last year, experts from CO₂ Sciences, Columbia University and Valence Strategic came together to develop a roadmap.

That document, Carbon Dioxide Utilization ICEF Roadmap 1.0, released at the UNFCCC Marrakesh Climate Change Conference in 2016, surveyed the commercial and technical landscape of CO₂ conversion and use. The document provided extensive background and analysis and has helped to provide a foundation for additional studies, including this one.

This roadmap is meant to complement and expand upon the work of its predecessor. Based in part on a workshop at Columbia University's Center on Global Energy Policy in July 2017, it explores three distinct categories of CO₂-based products, the technologies that can be harnessed to convert CO₂ to these products, and the associated research and development needs. It also explores the complicated topic of life cycle analysis—critically important when considering the climate impacts of CO₂ conversion and use—as well as policy tools that could be used to promote CO₂-based products.

The authors of this new roadmap hope that it will prompt others to explore these topics as well, and to increase the rigor and robustness of both life cycle analyses and techno-economic assessments. The CO₂-derived product markets will only benefit from more scrutiny and additional analytic work, and we invite others to join us in cultivating an open, transparent and actionable set of results that can undergird future standards and business transactions in CO₂ conversion and use.

Authors:

David Sandalow
Center on Global Energy Policy,
Columbia University
Chair, ICEF Innovation Roadmap
Project

Roger Aines
Lawrence Livermore National
Laboratory

Julio Friedmann
Lawrence Livermore National
Laboratory

Colin McCormick
Valence Strategic

Sean McCoy
Lawrence Livermore National
Laboratory

This roadmap was prepared to facilitate dialogue at the Fourth Innovation for Cool Earth Forum (Tokyo October 2017), for final release at COP-23 (Bonn November 2017).

Contents

| | |
|-----------|---|
| 1 | Chapter 1 Introduction and Overview |
| 7 | Chapter 2 Concrete and Carbonate Materials |
| 17 | Chapter 3 Commodity Chemicals |
| 29 | Chapter 4 Durable Carbon Materials |
| 37 | Chapter 5 Life Cycle Assessment |
| 45 | Chapter 6 General R&D Needs for CO ₂ Utilization |
| 49 | Chapter 7 Policy Options |
| 55 | Chapter 8 Findings and Recommendations |

Chapter 1:

Introduction and Overview

The Paris Agreement helped mobilize the global community behind the goal of limiting the increase in global average temperatures to less than 2°C above pre-industrial levels. Many studies have concluded that this can be achieved with conventional mitigation measures,¹ including a significant contribution from carbon capture and storage (CCS).² Other studies have concluded that the Paris Agreement goals require going beyond traditional mitigation approaches and must include removal of carbon dioxide (CO₂) from the air and oceans, as well as geological storage or conversion to minerals.³

As with other technologies, including clean energy technologies,⁴ broad deployment of CCS would reduce costs, improve performance, and earn public confidence.⁵ Following the ratification of the Paris Agreement, there has been increased attention on CO₂ utilization (CO2U), which is the utilization of CO₂ for an economically beneficial purpose. Traditionally, CO2U has primarily included enhanced oil recovery and the co-production of water; both of these applications use large volumes of CO₂ and result in its geological storage. However, interest in CO2U has increasingly become focused on the conversion of CO₂ into other products, such as cement, synthetic fuels and plastics.

Many see CO2U as a way to offset the cost of CO₂ capture, which is the costliest part of the CCS chain. Others note that it may improve public perception of and acceptance of CCS. Both of these would be the result of revenues and economic benefits from the captured CO₂ that are absent from CCS today. The combination of CO2U with CO₂ removal from the air and oceans could also produce durable materials and fuels that are not based on fossil carbon and encourage a “circular economy”.⁶ Finally, it is worth noting that political opinion about CO2U is often less contentious than the combination of CO₂ capture with geologic storage because of potential revenues and other economic benefits.

The growth of interest in CO2U over the last two years has been due in part to the clarity that the Paris Agreement provides regarding a carbon budget and the relatively short time available to meet stabilization goals. In addition, the recent rapid reduction of costs for many renewable sources (notably solar and wind) has made low-cost, near-zero-carbon electricity abundant in both volume and geography. In some markets this has led to electricity being available at very low or even negative prices,⁷ and even curtailment of renewable generation at times.⁸ Since renewable electricity is increasingly cheap, interest has grown dramatically in potential applications—such as CO2U—that can harness this abundance in an economically and environmentally beneficial way.

The landscape of CO2U is complex and diverse. It involves a wide array of applications (e.g. adding CO₂ to greenhouses, conversion to liquid fuels), technologies (e.g. electrochemical conversion using fuel cells, thermal catalysis), energy requirements (i.e. exothermic vs. highly endothermic), and settings (i.e. large industrial sites vs. distributed applications). Since the field of study is relatively young and immature, there is only a limited amount of existing analysis regarding potential markets for products, climate benefits, additional benefits, and the volumes of CO₂ used or potentially to be used.

It appears that there is enough potential and opportunity to expand commitment of resources into CO2U. It also appears that planning and investment decisions remain hampered by a lack of information, the dynamic nature of the technology and the markets, and the changing policy landscape. Because of this, it will be important to continually revise and update roadmap studies like this one.



What is CO₂ utilization?

As it sounds, CO₂U is the use of CO₂ to produce or generate economically valuable products or services. The potential range of applications is very large and includes greenhouses, organic farming, conversion of CO₂ to fuels or chemicals, conversion to long-lived solids (e.g. plastics, carbon fiber, graphene), and conversion to carbonate minerals.

CO₂ -EOR

CO₂-based enhanced oil recovery (CO₂-EOR) is by far the most well-understood form of CO₂U. There is a well-established body of practice, commerce and law around CO₂-EOR, and the technology is mature. Today, roughly 17 million tons/year of anthropogenic CO₂ are used for EOR.⁹ While there remains debate over the use of CO₂-EOR as a climate mitigation option, various analyses have shown that it could be beneficial and it is represented in economic and analytical models.¹⁰ Many governments, companies and investors see CO₂-EOR as a critical path for early CCS adoption since it provides revenues, tax receipts, jobs and large-volume offtakes.¹¹ For these reasons, CO₂-EOR will not be considered further in this report.

Non-EOR applications

Because the non-EOR applications for CO₂ conversion are so varied, the technology is also diverse. In addition, many CO₂ conversion technologies are relatively early in their development, so a plethora of options and pathways exist today that may become technically or commercially viable in the future. The Carbon Dioxide Utilization Roadmap 1.0 reviewed and featured many of the most important CO₂U pathways and markets.¹² These include:

- **Minerals:** CO₂ can react with a range of minerals to form carbonate minerals, like calcite or magnesite. Their uses include pharmaceutical feedstocks and building materials like aggregate.
- **Concrete:** In some cases, CO₂ becomes a new or substitute feedstock in the concrete production process; in other cases, CO₂ is used to cure or process cement.
- **Fuels:** With added energy, CO₂ can be converted to any carbon-based fuel, including diesel, jet fuels, ethanol and natural gas.

- **Chemicals:** Similarly, with added energy, CO₂ can be converted to a wide range of organic chemicals, including methanol, ethylene, carbamates and others. These may be used directly, or as feedstocks for production of other products (e.g. plastics).
- **Polymers:** It is possible to polymerize CO₂ to form plastics and resins directly.
- **Carbon fibers and composites:** Either directly or indirectly via CO₂-based chemical intermediaries, one can form carbon fibers, carbon composites, and other long-lived materials (like graphene).

These products all have different price points, market volumes and performance requirements. They are also used in different ways, have different lifetimes and are disposed of differently, making evaluation of their emissions impact complicated. Many of these applications will have specific geographic regions of early production or adoption based on local conditions and resources.

It is important to note that this report doesn't consider CO₂ conversion pathways that depend on photosynthesis by living organisms (e.g. plants, algae). In part, this is because such biomass-based pathways are used widely today (e.g. bioethanol from corn and sugarcane) and continue to be the focus of research and development, which means that there is a wealth of prior and current work to frame considerations.¹³ Roadmaps and similar strategic plans also already exist for bioenergy.¹⁴ In contrast, direct CO₂ conversion via non-biomass routes is less well explored, less mature, and lacks a comprehensive review of the opportunities and challenges.

Recent assessments and analysis

As mentioned above, recent and rapid growth in interest around CO₂U has prompted efforts to support investments in both R&D and deployment into markets. For example, CO₂U is a specific topic mentioned under Mission Innovation, and is part of the set of grand challenges taken up within the multinational framework.¹⁵ The Oil and Gas Climate Initiative recently announced a dedicated annual R&D fund, a portion of which is focused on CO₂U.¹⁶ The European Commission has begun a new effort under the Horizon 2020 umbrella,¹⁷ and is providing funding to a set of institutions to develop assessments for CO₂U.

Similarly, following a review of these and other studies, as well as the work in the first ICEF roadmap, several uncertainties and knowledge gaps appear prominent:

- **Costs:** Even for a relatively restricted class of CO₂ conversion approaches (e.g. CO₂ mineralization and conversion to aggregate), little is known about the current or likely costs, including first-of-a-kind (FOAK) or Nth-of-a-kind (NOAK). Cost uncertainties flow from the wide range of technical approaches, a paucity of published literature and confidentiality among companies.
- **Market potential:** The sizes of the individual markets for specific CO₂U applications vary widely. Moreover, there is no clear sense within a given market of the ability to compete on price or displace incumbents, in part because non-cost factors such as performance and standards affect analysis and comparisons.
- **Climate benefit:** The size of the market and rate of market penetration certainly affects the potential climate benefit of a CO₂U technology. So do the specifics of a technical approach (for example, how much carbon is used to make a pound of plastic), the source of the CO₂, the energy needed to convert it, and many other factors. Ultimately, these factors must be considered in an integrated fashion, using life cycle analysis (LCA).
- **Potential for disruption:** Some markets today are very small, e.g. carbon fiber. However, if carbon fiber can be made cheaply using CO₂ as a feedstock, it could potentially replace many other materials in the market (e.g. rolled steel or aluminum), greatly increasing the market size.
- **Policy:** Many countries, states, cities, and even companies are considering policy shifts in CO₂U. The range of policies under consideration today is wide, including tax credits, reporting requirements, procurement mandates, market mandates (such as a portfolio standard) and shareholder actions. Policy shifts could affect all the other uncertainties.

This report is an attempt to provide some clarity to this dynamic technology and market landscape.

Focus on case studies and LCA

Making sense of the current landscape of CO₂U opportunities, technologies and markets remains difficult. The enormous range of potential uses,

product prices, conversion costs, and technology options—on a dynamic landscape of technology and policy development—complicates many straightforward approaches to comparative analysis, quantitative or qualitative.

Case-study methodology represents complexity well and provides a way to achieve depth of investigation. This report focuses on a set of case studies, each reflective of a different set of technologies and markets, in an attempt to represent a range of technologies, market conditions, and potential outcomes. These are:

- **Concrete and carbonate materials:** This case looks at CO₂U pathways with large market potential and helpful thermodynamics (little energy is needed to make these products). The market value of the products is relatively low. Given technical and market readiness, this represents an opportunity for near-term deployment (3-10 years).
- **Commodity chemicals:** This case looks at CO₂U pathways with modest markets and CO₂ volumes. In some cases, the technology is fairly mature; less so in others. In most cases, substantial energy inputs are required. However, the value of some of these intermediates is quite high. These chemicals are anticipated as feedstocks for long-lived products (e.g. polymers). Given technical and market readiness, this represents an opportunity for near- to medium-term deployment (5-20 years).
- **Durable carbon materials:** This case looks at CO₂U pathways that today represent relatively small markets (e.g. carbon composites or graphene). Many of the conversion technologies for direct single- or multi-stage conversion of CO₂ are nascent and very early in development. However, the market potential of these materials may be quite large, and the market value of these products ranges from moderate to very high. Given technology and market readiness, this represents a long-term set of opportunities.

Estimating the climate benefits for these different approaches and products is difficult. Differentiated and specific information inputs are needed to execute an accurate life cycle analysis (LCA) for any specific production pathway, and the scope, boundaries, and detailed methodological assumptions of LCA have a significant impact on the result. Since a critical

market and environmental value of CO₂U is the net carbon reduction, this report features a review and discussion of both the current state of the art and the key challenges in undertaking precise and accurate estimation of CO₂U LCA. An important conclusion is the need for guidelines and standards for accounting CO₂U carbon balances. Standards (such as those established by the International Organization for Standardization) will help facilitate market adoption, as well as undergird policy decisions and the development of regulations. However, given the intrinsic complexity and early stage of CO₂U technologies and markets, it may prove challenging to achieve precision and accuracy for LCA of early-stage pathways, and guidance may need to be adapted over time to address the lessons from such analyses. A further point to emphasize is that LCA should be incorporated in the technology development process from an early stage, for example, through “hotspot” and improvement analyses. As the technology matures, these studies should be progressively refined, providing both guidance for future research directions and an increasingly useful assessment of a technology’s climate impact.

¹ Otmar Edenhofer et al., eds., *Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press, 2014).

² IEA, *Energy Technology Perspectives 2015: Mobilizing Innovation to Accelerate Climate Action* (Paris, France: International Energy Agency, 2015); Elmar Kriegler et al., “The Role of Technology for Achieving Climate Policy Objectives: Overview of the EMF 27 Study on Global Technology and Climate Policy Strategies,” *Climatic Change* 123, no. 3–4 (April 1, 2014): 353–67, doi:10.1007/s10584-013-0953-7; Detlef P. van Vuuren et al., “The Role of Negative CO₂ Emissions for Reaching 2 °C—insights from Integrated Assessment Modelling,” *Climatic Change* 118, no. 1 (2013): 15–27, doi:10.1007/s10584-012-0680-5.

³ UNEP, “The Emissions Gap Report 2016” (Nairobi, Kenya: United Nations Environment Programme, 2016), http://wedocs.unep.org/bitstream/handle/20.500.11822/10016/emission_gap_report_2016.pdf

report_2016.pdf; Benjamin M. Sanderson, Brian C. O’Neill, and Claudia Tebaldi, “What Would It Take to Achieve the Paris Temperature Targets?,” *Geophysical Research Letters* 43, no. 13 (July 16, 2016): 7133–42, doi:10.1002/2016GL069563; Pete Smith et al., “Biophysical and Economic Limits to Negative CO₂ Emissions,” *Nature Climate Change* 6, no. 1 (January 2016): 42–50, doi:10.1038/nclimate2870.

⁴ Timothy J. Foxon, “Stimulating Investment in Energy Materials and Technologies to Combat Climate Change: An Overview of Learning Curve Analysis and Niche Market Support,” *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 368, no. 1923 (2010): 3469–83, doi:10.1098/rsta.2010.0106.

⁵ IEA, *Energy Technology Perspectives 2015*.

⁶ F. S. Zeman and D. W. Keith, “Carbon Neutral Hydrocarbons,” *Philosophical Transactions of the Royal Society a- Mathematical Physical and Engineering Sciences* 366, no. 1882 (November 2008): 3901–18, doi:10.1098/rsta.2008.0143.

⁷ A. Hove and K. Mo, 2016, *Going for Gold: Championing Renewable Integration in Jing-Jin-Ji, Best practices from Germany and Texas*, Paulson Institute, <http://www.paulsoninstitute.org/economics-environment/climatesustainable-urbanization/research/going-for-gold-championing-renewable-integration-in-jing-jin-ji/>

⁸ CAISO. Wind Solar Real-time Dispatch Curtailment Report Oct 04 2016, page 4/5

⁹ NEORI, “Carbon Dioxide Enhanced Oil Recovery: A Critical Domestic Energy, Economic, and Environmental Opportunity” (Washington, DC: National Enhanced Oil Recovery Initiative, 2012).

¹⁰ IEA, “Storing CO₂ through Enhanced Oil Recovery” (Paris, France: International Energy Agency, 2015), <https://www.iea.org/publications/insights/insightpublications/storing-co2-through-enhanced-oil-recovery.html>.

¹¹ National Coal Council, “CO₂ Building Blocks: Assessing CO₂ Utilization Options” (Washington, D.C.: National Coal Council, 2016), <http://www.nationalcoalcouncil.org/studies/2016/NCC-CO2-Building-Block-FINAL-Report.pdf>; Stefan Bachu et al., “Technical Challenges in the Conversion of CO₂-EOR Projects to CO₂ Storage Projects” (Washington, DC: Carbon Sequestration Leadership Forum (CLSF), 2013).

¹² Issam Dairanieh et al., “Carbon Dioxide Utilization (CO2U) – ICEF Roadmap 1.0” (Tokyo, Japan: ICEF Innovation Roadmap Project, 2016), http://www.icef-forum.org/platform/upload/CO2U_Roadmap_ICEF2016.pdf.

¹³ Felix Creutzig et al., “Bioenergy and Climate Change Mitigation: An Assessment,” GCB Bioenergy 7, no. 5 (September 1, 2015): 916–44, doi:10.1111/gcbb.12205.

¹⁴ IEA, “Technology Roadmap: Biofuels for Transport” (Paris, France: International Energy Agency, April 20, 2011), <https://www.iea.org/publications/freepublications/publication/technology-roadmap-biofuels-for-transport.html>; IEA, “Technology Roadmap: Bioenergy for Heat and Power” (Paris, France: International Energy Agency, May 29, 2012), <https://www.iea.org/publications/freepublications/publication/>

technology-roadmap-bioenergy-for-heatand-power-.html.

¹⁵ Mission Innovation, “Carbon Capture Innovation Challenge – Mission Innovation,” Mission Innovation, accessed September 11, 2017, <http://mission-innovation.net/our-work/innovation-challenges/carbon-capture-challenge/>.

¹⁶ OGCI, “OGCI Climate Investments,” Oil and Gas Climate Initiative, accessed September 11, 2017, <http://www.oilandgasclimateinitiative.com/climateInvestments.html>.

¹⁷ European Commission, 2016, Research and Innovation Participant Portal, Horizon 2020 Prize for CO₂ Reuse, <http://ec.europa.eu/research/participants/portal/desktop/en/opportunities/h2020/topics/ice-prize-co2reuse-01-2016.html>

Chapter 2: Concrete and Carbonate Materials

Introduction

The largest near-term opportunity for utilizing CO₂ is in cement and the aggregates used in concrete materials.¹ This is because of the extraordinary volume of these materials used commercially, their permanence, and the favorable chemistry involved. For these reasons, this chapter will consider CO₂U for cement and aggregates as a near-to-market case study, illustrating how policy can support the further development and deployment of this technology.

Cement, along with aggregate and water, are the main components of concrete (see **Box 2.1**). The 2016 market for concrete was around 30 billion tons (Gt) of product, based on the global cement market size of approximately 4 Gt.² The Carbon Dioxide Utilization Roadmap 1.0 estimated that the total market for concrete would grow to about 40 Gt in 2030.³ It further estimated that the worldwide aggregates market was between 25 Gt and 35 Gt in 2015, and would grow to about 50 Gt of product in 2030.

There are several approaches to incorporating CO₂ into concrete. In direct utilization systems, the amount of CO₂ consumed varies between 0.15%⁴ and 24%⁵ by weight of traditional Portland cement used, or 0.02% to 3% by weight of concrete. Applying direct utilization systems to all concrete produced in 2016 would, thus, create a demand between 10 MtCO₂ and 1000 MtCO₂,

globally, and up to 1200 MtCO₂ in 2030. Aggregates could consume on the order of several billion additional tons of CO₂ if they were partially made from CO₂.⁶

These large market volumes make concrete and aggregates an attractive target for CO₂U. In addition, these products result in an effectively permanent means of sequestering CO₂: mineral fixation. This means that they have a clear leg up relative to other CO₂-based products in terms of climate impact. Additionally, this application takes advantage of two important characteristics of CO₂:

1. CO₂ is a very low-energy molecule, meaning that converting it to most other relevant molecules (such as liquid fuels) requires adding significant amounts of energy (refer to Section 3). However, the form of carbon that makes up cements and aggregates (carbonate, CO₃²⁻) is an even lower-energy molecule. If the conditions are properly established, CO₂ can be chemically converted into carbonate without the need for external energy to drive the reaction. This is extremely important for making large volumes of material, which could be prohibitively expensive and emissions-intense if there were a need to add energy to the reaction.
2. The second characteristic is seemingly pedestrian but important: CO₂ weighs a lot. This is an under-appreciated requirement for many uses of concrete, where the sheer mass of material is an important building element (see **Figure 2.1**).

These characteristics have led to several proposed uses of CO₂ as part of the actual binding material (cement), and as a component of the filler (aggregate) that makes up most of concrete by mass. Both cement and



Figure 2.1. The concrete pylons of the San Francisco Bay Bridge counter the weight of the suspension bridge and vehicles by simply being heavier. <https://www.pexels.com>.

BOX 2.1 Cement and Concrete

Concrete that is used in the construction industry is a mixture of cement (sometimes referred to as binder), water, and solid aggregates such as sand, gravel, and crushed stone (sometimes referred to as filler). A typical mixture by volume is 10-15% cement, 15-20% water and 60-75% aggregate. Manufacturing cement involves heating limestone (calcium carbonate) and clay materials (primarily alumino-silicates) in a kiln to form a material known as clinker, which is then ground into a fine powder. When this is mixed with water and aggregates, a series of chemical processes (“curing”) converts the cement powder into interlocking crystals, which grow stronger over time. These crystals give concrete very good compression strength—so it can support a lot of weight—but poor tension strength, meaning that it cannot resist being pulled apart unless other materials are added, such as steel (“rebar”). Since the hydrated calcium oxide found in cement is very reactive with CO₂—in fact, CO₂ is naturally taken up by the cement over time—it is possible to return some of that CO₂ to the product.



aggregate applications require the carbonate ion to be balanced by a cation with two positive charges: most often calcium (Ca⁺⁺) or magnesium (Mg⁺⁺). Both cation-carbonate ion pairs are also very common minerals in nature: calcium carbonate is limestone or marble, and magnesium carbonate, while less common, is a natural material called magnesite with comparable properties to limestone.

The requirement that cations balance the charge on the carbonate ion CO₃²⁻ is the most important challenge to making carbonates and cements. Divalent ions (+2 charged) are strongly preferred; unfortunately, they are not broadly available. The largest commercial source of +2 calcium is limestone, but extracting the calcium cations from this rock releases carbon dioxide, making it impossible to achieve any net climate benefit. Monovalent ions like sodium and potassium (Na⁺ and K⁺) can also balance the charge and be obtained at much lower cost and emissions footprint. However, using them as cations usually results in water-soluble solid products of limited commercial use as construction materials.

One possible alternative source of calcium and magnesium is seawater, which is a very large resource. This is an active area of research.⁷ Another possible source is ultramafic rocks or (in lower concentrations) basaltic lava. Transporting these heavy rocks to a site where they could be reacted with CO₂ is the primary economic impediment of this approach, but could be overcome in strategic locations where CO₂ sources

and markets are also nearby. Slags and other alkaline industrial wastes also contain the appropriate ions, and at scales of a few hundred million tons, may be extremely valuable feedstocks to make carbonate solids. Use of industrial wastes may also be viewed as a means of waste treatment, resulting in stabilization of metals that might otherwise be hazardous in the environment.⁸

The use of these compounds as building materials dates back thousands of years, and there is widespread experience with their performance in such applications, including their non-toxic and long-lasting natures. Meeting expectations (and standards) for their performance—particularly tensile and compressive strength metrics—is the most important aspect of making new materials containing CO₂ (see Box 2.2). Understanding the impact of CO₂ addition to the products and gaining widespread acceptance of the practice is, thus, critical. On the other hand, it is widely accepted that the nature of the materials and their use means that carbon fixed in cements and aggregates is likely to remain in this form indefinitely, keeping it out of the atmosphere for hundreds or even thousands of years.

State of the technology

More than 20 organizations are actively engaged in commercializing processes to convert CO₂ to carbonate products for the construction sector (**Figure 2.2**). CO₂-based aggregates, concrete, and pre-cast concrete

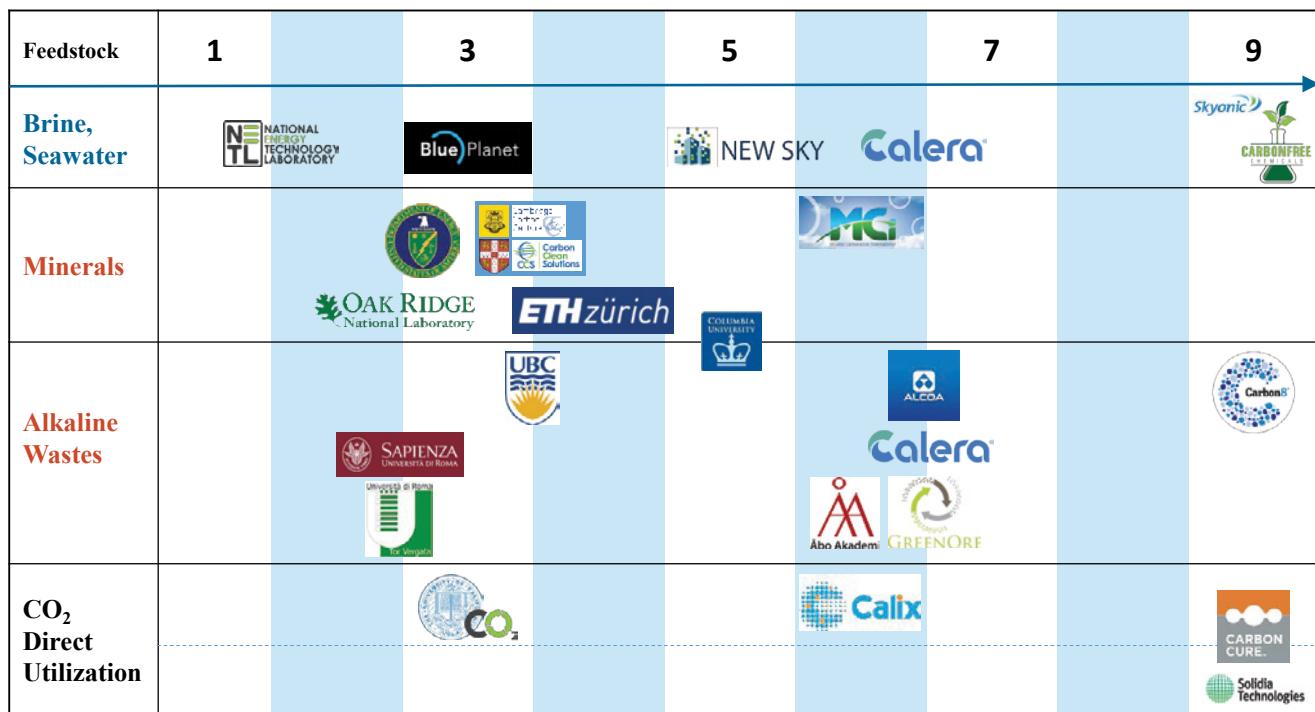


Figure 2.2. Stages of technology development for concrete and carbonate materials. (credit: Sean Zhou, Columbia University)

products are commercially available today. The primary difference among the technology pathways is the source of the cation to pair with the carbonate ion.

- Pathways using calcium from seawater are primarily using electrochemical means to separate the calcium from seawater, although if done improperly this approach can release CO₂ from seawater as well and negate the climate benefit.
- Mineral sources are inherently easier to use, but require transport of either rock to the carbonation site, or carbonate product to the construction site. In some cases, they also require additional capital and energy for grinding and processing mineral feedstocks.
- Approaches using alkaline wastes are the most advanced category because the calcium and magnesium ions in wastes like iron slag are concentrated (up to 40% by weight) and are more climate-friendly to use, since their utilization only releases oxygen as the cations are changed from oxygen-compensated (CaO, MgO) to carbonate (CaCO₃, MgCO₃).
- A final category follows a slightly different approach: instead of attempting to make a carbonate product, some organizations are replacing water in cement

with carbon dioxide. Two companies, CarbonCure and Solidia Technologies, currently sell commercial products in this space.

Technical and economic limitations

Although the potential markets are large and much of the fundamental chemistry and physics is well-understood, all approaches face some sort of technical challenge for economic viability. Some of these issues involve pre-processing of feedstocks, including transportation and size reduction (crushing) costs. Other issues involve adding energy or new chemical pathways to accelerate key reactions, but with additional capital or operating expense. These challenges all appear surmountable, either through improving technical aspects of the work (e.g. higher efficiency, lower equipment cost) or improving the economics of the process or products. The companies involved are working to overcome these obstacles.

Seawater-Sourced Calcium. This approach benefits from a nearly unlimited source of calcium from seawater, which is routinely available near large industrial sources of CO₂. A related option is to obtain calcium from brines found deep in sedimentary basins (where oil reservoirs are also found), many of which originally came from seawater. These sources have

calcium ions compensated by chloride ions. If the calcium ions are to be used elsewhere, the chloride ions must either be converted to neutral chlorine gas, a useful industrial product, or be compensated by some other ion by an 'ion exchange' process.

Calera Corporation demonstrated considerable progress in this area, ultimately developing an advanced electrolysis system for extracting calcium and chlorine, that proved economic on the basis of the sale of the chlorine product.⁹ An innovative aspect of this process was the use of the calcium carbonate as a supplemental cementing material by encouraging the creation of interlocking crystals that provide valuable tensile strength. Calera has demonstrated production of a fiber cement board from this process.¹⁰ However, although there is a nearly unlimited source of calcium, the profitability of this process depends on the sale of chlorine gas, which has a market of about 60 million tons per year,¹¹ much smaller than the potential cement and aggregate market.

Technology development pathways in this area focus on reducing energy expense. They include more efficient electrolysis methods and innovative ion-exchange processes. Additional research on converting byproduct wastes into valuable products would also improve the economics.

Mineral-Based Calcium. A large quantity of available calcium appropriate for carbonation exists in the stockpiles of asbestos-, nickel- and diamond-mining wastes,¹² but almost no commercial work exists to turn these feedstocks into construction materials. This is principally because of geographic mismatch. In general, large industrial CO₂ sources do not exist near most mines creating this kind of waste, and the cost of transporting this material makes it economically unviable. However, these wastes carbonate readily—even without any encouragement beyond the original grinding process used to extract the product. Thus, one approach is to use these wastes to absorb CO₂ from the atmosphere, but not immediately convert the result into a valuable product. The DeBeers company has announced that they will carbonate their mine tailings in order to offset the CO₂ emissions associated with diamond-mining operations.¹³

Basalt rock found in many volcanic regions of the world could also be used as a source of mineral-based calcium. One cubic kilometer of basalt contains

enough magnesium and calcium to capture one billion tons of CO₂. This is being investigated as a means of subsurface storage in the United States and Iceland, but no schemes to harvest that calcium as a precursor to building material have yet been announced.

This is due to the relatively lower concentration of magnesium and calcium in basalt (5-10%) compared to the relatively higher concentrations in asbestos-, nickel- and diamond-mining waste (10-50%).

Technology development pathways in this area include the development of high-value products that could be transported long distances at a profit. Construction materials would likely need to be decorative or high-functioning to meet this criterion, rather than the bulk cements and aggregates already discussed. Alternatively, a sufficiently high carbon price could make aggregate sourced in mine wastes profitable, leading to early introduction of these products into the market.

Alkaline Industrial Waste-Sourced Calcium, Magnesium and Iron. An extensive literature exists in this area,¹⁴ and a number of commercial ventures have been undertaken. Industrial wastes such as steel slag contain large amounts of calcium, magnesium and even iron, which can also participate in carbonation reactions. These materials are generally land-filled and using them productively could create economic benefits in addition to the value of the new products, due to reduced landfill costs. Many authors include a large variety of industrial wastes, such as fly ash from coal plants, in the list of potential starting materials, but the degree of reactivity varies greatly as does the concentration of divalent ions required to bind to the carbonate. Worldwide sources of highly reactive material appear to be capable of consuming CO₂ on the order of 100 million tons per year.

Most of these materials require some significant pre-treatment to react at industrially significant rates. Many studies have examined heat treating to "activate" these wastes, making them react with CO₂ in a matter of seconds. This commonly introduces significant cost, both in terms of capital and operating expense. An important exception is red mud from aluminum production, which contains iron oxide, and reacts spontaneously with CO₂ in waste ponds. However red mud also contains other metallic oxides which do not spontaneously react into a usable

product, adding a cost for processing. This points out a significant limitation in the use of industrial wastes: they often require significant separation before or after use.

Technology development pathways include combining activation and separation approaches—a significant R&D challenge. For example, activation could be enhanced through the development of new catalysts and low-cost reactors.

Direct Utilization of CO₂. The final major category concerns producers that take a different approach—replacement of water in cements with CO₂. This can occur in two different ways: CO₂ can either be added to conventional cements during the grinding phase, or it can be added during the final curing of the cement by replacing some water with CO₂. In addition, both approaches result in a reduction in the amount of clinker required in the final mixture (to achieve a consistent strength), thus leading to reduced emissions from the production of the cement.

CarbonCure is pursuing technology based on this approach that can be retrofitted to conventional “ready-mix” concrete plants.¹⁵ CO₂ is injected into the concrete mix at the plant, and as the concrete cures, the CO₂ is permanently mineralized. This takes advantage of the fact that the primary binding phase, calcium oxide, was created by removing CO₂ from limestone, which can be reversed, reducing the overall carbon footprint of the cement while still providing the necessary new formation of minerals required to bind the cement and aggregate together. The resulting concrete has been measured to have better compressive strength performance than that made with ordinary Portland cement.¹⁶

Solidia Technologies has taken this approach one step further by changing the makeup of the ‘clinker’ that comes out of the cement kiln.¹⁷ By using more silica-rich materials, they achieve a cement mixture that binds with more CO₂ and can be used to make high-strength pre-cast materials, as well as reducing both the consumption of limestone and the temperature required in clinker production. However, this cement must be cured in a sealed environment, limiting it to precast objects for now.

The research pathways in this case focus on process developments to increase the amount of CO₂ absorbed while still maintaining a strong and competent product. Understanding changes in performance properties

resulting from CO₂ addition is currently a major research and development objective. Methods to apply CO₂ during curing of large construction concretes could greatly expand the applicability of CO₂U, as could easier means to more directly measure the amount of CO₂ that has been taken up by concretes.

Sodium and Potassium-Compensated Materials. The use of +1 ions to combine with carbonate results in products that are not permanent building materials, but rather products used as industrial chemical feedstocks and animal supplements. Skyonic¹⁸ is developing technology that takes advantage of a coupled process that simultaneously removes CO₂ and other contaminants such as sulfur oxides.

Market considerations

The billions of tons of CO₂U potential in cement and aggregate represent low-margin, highly standardized markets that are difficult to penetrate with new products.¹⁹ Successful businesses to date have focused on making incremental changes to traditional concrete formulation to minimize the acceptance challenges, or on niche markets. Significant penetration into the billion-ton global cement market will be very slow by this method. On the other hand, use of carbonate as aggregate does not face such significant hurdles to market entry, but does face significant cost pressures. With gravel costs typically in the vicinity of \$50/ton even in high-priced markets like California, it is unlikely that an industrial process making a CO₂-based product will be competitive purely on price. This will be true in most major construction markets absent policy support. Regulatory considerations are critical (see **Box 2.2**).

The billions of tons of potential market and carbon mitigation also appear to require significant technology development to be accessible. Direct CO₂ utilization as an additive in conventional products is the most technologically mature approach, and if regulatory acceptance can be achieved, this approach could utilize several percent CO₂ by weight of concrete in pre-cast applications where the “green” nature of the product is valued. With the EU, United States, and China all showing signs of such valuation, this market will probably expand. Particularly in the EU, cement manufacturers are reporting their carbon footprints and competing to reduce them. This effort is mainly focused on more efficient clinker production and using

BOX 2.2 Regulations and Standards²²

CO₂ utilization can be pursued to create products using new methods, materials or feedstocks. In many instances, the products will need to adhere to existing codes and standards to be accepted in the marketplace. Often, there can be barriers within the codes and standards framework that discourage products made using new technologies.

Codes and standards are typically overseen by members of government and industry, and developed by consensus-based and voluntary committees. Often, there are few incentives to update or expand existing standards. Further, even if the willingness exists, the changes to the regulatory framework can occur slowly. A process extending to 10 years is not unusual. The route to acceptance under codes and standards can be long enough to discourage the entrance of new technology into the market.

—Sean Monkman, Carbon Cure



less clinker, which has resulted in a 22% reduction in carbon footprint for the European manufacturer Heidelberg Cement since 1990.²⁰ Efforts such as this will have a significant impact on overall emissions, and as efficiency limits are reached, these corporations may be expected to take on new carbonation approaches to continue their reductions. Expansion of those ambitions to the Chinese market, at nearly 2 billion tons of supply,²¹ would have a significant impact on world CO₂ emissions.

Life-cycle analysis considerations

Production of concrete is very emissions-intensive, releasing approximately 240 kgCO₂-eq to 320 kgCO₂-eq per m³ (or approximately 104 to 139 kgCO₂-eq/t cement).²³ The production of clinker is responsible for 90%–98% of cement greenhouse gas emissions. The main contributors to emissions from clinker manufacturing are the release of CO₂ during calcination of limestone (i.e. calcium carbonate, CaCO₃) to produce calcium oxide (CaO), and the fuel emissions associated with heating the raw materials to over 1400 °C during sintering (i.e. formation of calcium silicates). Reducing clinker use or changing the cement chemistry to reduce limestone use or the maximum temperature required—while still providing a finished concrete that meets or exceeds required measures of performance—are clear means to reduce emissions. Both industrial routes to direct CO₂ utilization achieve a lifecycle emissions benefit by reducing limestone use.²⁴

Solidia may also achieve a benefit by using a cement chemistry that requires a lower sintering temperature (approximately 1200 °C).²⁵

In addition to the above lifecycle emissions benefits, direct CO₂ use results in the accelerated uptake of CO₂ by the concrete. This is referred to as “accelerated” because the mixed calcium hydroxide ‘gels’ that make up the binding phase in conventional concrete naturally absorb CO₂ from the atmosphere at very slow rates. In a case study of the conventional cement lifecycle in the Nordic countries—including crushing of concrete after demolition—the authors estimate between 33% and 57% of the emissions from cement manufacture are later absorbed by the cement.²⁶ In a comparable study of the United States, in which the lifecycle excludes demolition and crushing, the authors estimate that the concrete only reabsorbs about 8% of the manufacturing emissions.²⁷

The potential benefits of accelerated uptake in direct CO₂ utilization are twofold: CO₂ is removed more rapidly, and more CO₂ may be absorbed through natural carbonation than would otherwise occur. The first benefit may be particularly important, given that the large emissions from cement manufacture occur near the beginning of the lifecycle. Thus, the more rapidly the absorption offset occurs, the greater the climate benefit (Chapter 5 discusses accounting for time-dependent emissions in LCA). However, to date only one peer-reviewed estimate has been made of the emissions benefit of direct CO₂ use in concrete,²⁸

and this is clearly an area where additional analysis is needed.

In contrast, the lifecycle of CO₂-based aggregate production has been assessed in a handful of studies.²⁹ Collectively, these studies have considered ex-situ mineralization of two distinct categories of alkalinity sources: ultramafic minerals (i.e. olivine, serpentine and wollastonite) mined for use in the process; and various waste streams (fly ash, cement kiln dust, and steel slag). All but one of these studies³⁰ have assessed the emissions reduction potential of mineralization of CO₂ as the end goal, concluding that they result in a net emissions reduction. The single study that looked at the beneficial re-use of the CO₂-based aggregates concluded that it made only a small difference to the overall lifecycle emissions benefit because the avoided emissions from aggregate mining are small and the additional process steps required to prepare the CO₂-based aggregates for re-use offset much (or all) of the benefit. This is a significant difference from concrete, where reduction in use of Portland cement appears to be the driver of emissions reduction benefit.

The aggregate studies highlight that there is a great deal of variability between processes identified in the literature³¹ and between alkalinity sources.³² In fact, few of the processes under commercial development have publicly available, peer-reviewed LCA results. One of the existing studies also identifies ways to optimize CO₂-based aggregate production processes to maximize the emissions re-absorption benefit.³³ This latter finding is an excellent example of the way in which LCA results can be used to inform research and development (R&D).

Alternative cement formulations will not evolve on a linear path with one technology taking precedence. Alternative clinker, more efficient production of clinker, and supplementing conventional cement with CO₂-amended materials will move forward together. (**Figure 2.3**) In addition, there are multiple other opportunities to reduce greenhouse gas emissions from concrete manufacturing, some of which can be applied today (e.g. materials efficiency) and some of which are longer-term objectives for the industry (e.g. CCS).³⁴ Given the differences between the ways in

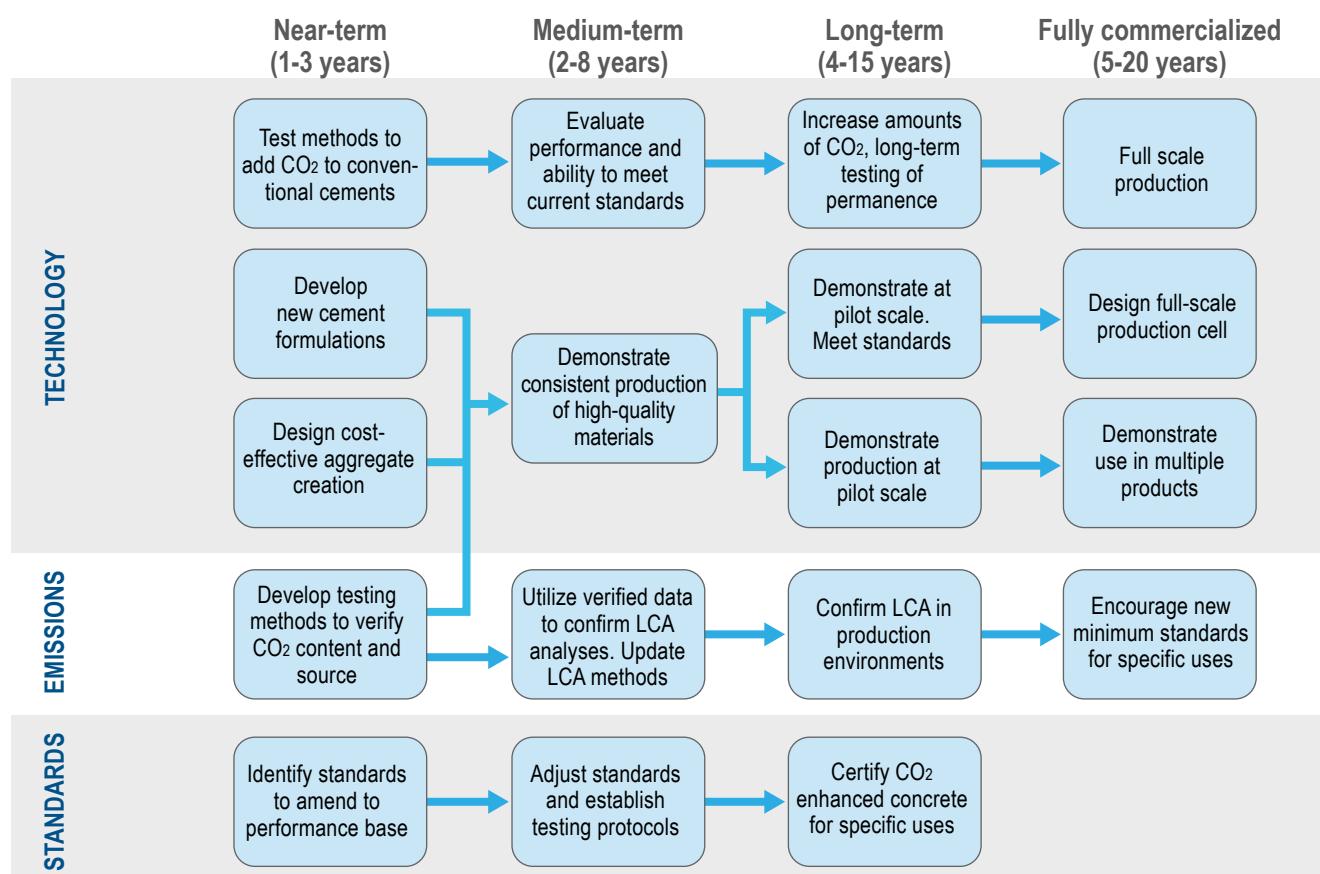


Figure 2.3. Conceptual roadmap for accelerating the development and certification of CO₂-enhanced concrete.

which concrete is manufactured and used regionally, the lowest-cost options to reduce emissions will vary. An important objective for industry bodies (e.g. World Business Council for Sustainable Development) and intergovernmental organizations (e.g. UNIDO, UNEP) should be the continued development of regional roadmaps that show the opportunities to incrementally reduce their emissions while creating value for the industry.

Recommendations/Conclusions

Cement and aggregate have a large market potential for CO₂ utilization, but that potential is in fact divided into smaller opportunities that require separate paths to full achievement.

Aggregate by itself appears to require direct incentives for CO₂ utilization to be economically viable. The methods by which CO₂ can be turned into industrially useful aggregate are well-established, and the costs always exceed the cost of conventional aggregate like gravel or even crushed stone. The “low-hanging fruit” in this area involves avoiding the cost of industrial waste disposal, which improves the market for cement kiln dust, iron slag, aluminum red mud and coal fly ash. It is likely, however, that the social acceptability of those methods will vary widely by market, with iron slag and aluminum red mud achieving much higher utilization because the value of the original product (iron and aluminum) is expected to stay high. R&D in the separation of undesirable contaminants will be crucial to achieve widespread market penetration for these products.

Cement and concrete alternatives and carbon footprint reductions are already being pursued to achieve “green” product distinctions. A critical need in this area is life cycle assessment that accurately includes the efficiency and carbon-utilization benefits as small proportions of CO₂ are added to products. This can have a multiplicative effect through the reduction of other raw materials.

The second, and perhaps dominant, need in this area is for demonstration projects that create large volumes of these alternative materials to aid in the regulatory evaluation and acceptance for materials that have critical construction requirements. Some early-market penetration can be expected in shop-built materials that can be tested by standard ASTM

methods today—this is an early-adoption pathway that is proving successful and can be expanded. Industry and government influencers should act to foster a regulatory environment that promotes a measured and fair process to ensure that products meet both quality and safety requirements yet innovative technologies can enter and compete in the marketplace without undue resistance.

Methods to evaluate the benefits and performance of site-poured cements and concretes do not appear to exist, and should be encouraged.

The overall lifecycle for concrete as it ages in use is not well understood, particularly when it is removed and reused as aggregate in new concrete, as is commonly the case. This may be an excellent opportunity to encourage more cement carbonation, and should be researched.

¹ Issam Dairanieh et al., “Carbon Dioxide Utilization (CO2U) – ICEF Roadmap 1.0” (Tokyo, Japan: ICEF Innovation Roadmap Project, 2016), http://www.icef-forum.org/platform/upload/CO2U_Roadmap_ICEF2016.pdf.

² USGS, “MINERAL COMMODITY SUMMARIES 2016” (Reston, VA: U.S. Geological Survey, 2016), <https://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf>.

³ Growth in the CO₂-based concrete curing market was 6.5 Gt, 10.5 Gt and 16.5 Gt in their scenarios. Dairanieh et al., “Carbon Dioxide Utilization (CO2U) – ICEF Roadmap 1.0.”

⁴ Sean Monkman and Mark MacDonald, “On Carbon Dioxide Utilization as a Means to Improve the Sustainability of Ready-Mixed Concrete,” *Journal of Cleaner Production*, n.d., doi:10.1016/j.jclepro.2017.08.194.

⁵ Warda Ashraf, “Carbonation of Cement-Based Materials: Challenges and Opportunities,” *Construction and Building Materials* 120 (September 1, 2016): 558–70, doi:10.1016/j.conbuildmat.2016.05.080.

⁶ Dairanieh et al., “Carbon Dioxide Utilization (CO2U) – ICEF Roadmap 1.0.”

⁷ Natasha and Lalasari 2017: <http://aip.scitation.org/doi/abs/10.1063/1.4974443>, PNNL/ARPA-E: <https://arpa-e.energy.gov/?q=slick-sheetproject/extracting-magnesium-seawater>.

⁸ Peter J. Gunning et al., "Secondary Aggregate from Waste Treated with Carbon Dioxide," *Proceedings of the Institution of Civil Engineers - Construction Materials* 164, no. 5 (October 1, 2011): 231–39, doi:10.1680/coma.1000011.

⁹ Scientific Synthesis of Calera Carbon Sequestration and Carbonaceous By-Product Applications Consensus Findings of the Scientific Synthesis Team January 2011 Co-Chairs Durwood Zaelke, Oran Young, & Stephen O. Andersen Donald Bren School of Environmental Science and Management University of California, Santa Barbara

¹⁰ Carbon Mineralization by Aqueous Precipitation for Beneficial Use of CO₂ from Flue Gas Final Scientific/ Technical Report Principle Investigators Martin Devenney Ryan Gilliam Project Director Randy Seeker Report Date: June 2015 U.S. Department of Energy National Energy Technology Laboratory Carbon Capture and Sequestration from Industrial Sources and Innovative Concepts for Beneficial CO₂ Use Award: DE-FE0002472 Reporting Period Start: January 15, 2010 Reporting Period Stop: June 30, 2015 Calera Corporation 7697 Highway One at Dolan Road Moss Landing, California 95039

¹¹ Chlorine Market: Global Industry Analysis and Opportunity Assessment 2015-2025. Future Market Insights. <http://www.futuremarketinsights.com/reports/chlorine-market>

¹² Strategizing Carbon-Neutral Mines: A Case for Pilot Projects Ian M. Power, Jenine McCutcheon, Anna L. Harrison, Siobhan A. Wilson, Gregory M. Dipple, Simone Kelly, Colette Southam and Gordon Southam. *Minerals* 2014, 4, 399-436; doi:10.3390/min4020399

¹³ De Beers Pioneers Research Program to Make Carbon-Neutral Mining a Reality. <https://www.debeersgroup.com/en/news/companynews/company-news/de-beers-pioneers-research-programme-to-make-carbon-neutral-mini.html>

¹⁴ An Innovative Approach to Integrated Carbon Mineralization and Waste Utilization: A Review Shu-Yuan Pan, Andrew Chiang, E-E Chang, Yi- Pin Lin, Hyunook Kim, Pen-Chi Chiang *Aerosol and Air Quality Research*, 15: 1072–1091, 2015 CO₂ Mitigation Potential of Mineral Carbonation with Industrial Alkalinity Sources in the United States Abby Kirchofer, Austin Becker, Adam Brandt, and Jennifer Wilcox, dx.doi.org/10.1021/es4003982 | *Environ. Sci. Technol.* 2013, 47, 7548–7554 Alkaline residues and the environment: a review of impacts, management practices and opportunities Helena I. Gomes, William M. Mayes, Mike Rogerson, Douglas I. Stewart, Ian T. Burke *Journal of Cleaner Production* 112 (2016) 3571e3582 A review of mineral carbonation technologies to sequester CO₂ A. Sanna, M. Uib, G. Caramanna, R. Kuusik and M. M. Maroto-Valer *Chem. Soc. Rev.*, 2014, 43, 8049-8080

¹⁵ Sean Monkman et al., "Properties and Durability of Concrete Produced Using CO₂ as an Accelerating Admixture," *Cement and Concrete Composites* 74 (November 1, 2016): 218–24, doi:10.1016/j.cemconcomp.2016.10.007; "CarbonCure | Transforming the Space We Live in," accessed September 12, 2017, <http://carboncure.com/>.

¹⁶ Monkman et al., "Properties and Durability of Concrete Produced Using CO₂ as an Accelerating Admixture."

¹⁷ "Solidia Cement: Part One of a Two-Part Series Exploring the Chemical Properties and Performance Results of Sustainable Solidia Cement and Solidia Concrete" (Piscataway, NJ: Solidia Technologies, December 17, 2013), <http://solidiatech.com/wp-content/uploads/2014/02/Solidia-Cement-White-Paper-12-17-13-FINAL.pdf>; Ashraf, "Carbonation of Cement-Based Materials."

¹⁸ <http://www.carbonfreechem.com>

¹⁹ Karen L. Scrivener, Vanderley M. John, and Ellis M. Gartner, "Eco-Efficient Cements: Potential, Economically Viable Solutions for a Low-CO₂, Cement-based Materials Industry" (Paris, France: United Nations Environment Programme, 2016).

²⁰ <https://www.worldcement.com/europe-cis/17072017/heidelbergcements-sustainability-challenge/>

²¹ <https://dealbook.nytimes.com/2014/04/07/chinas-dominance-in-cement-has-little-effect-on-european-suppliers/> <https://www.worldcement.com/the-americas/17022017/us-cement-capacity-sufficient-to-meet-demand/>

²² Box text provide by Sean Monkman, CarbonCure.

²³ Sabbie A. Miller, Arpad Horvath, and Paulo J. M. Monteiro, "Readily Implementable Techniques Can Cut Annual CO₂ Emissions from the Production of Concrete by over 20%," *Environmental Research Letters* 11, no. 7 (2016): 074029, doi:10.1088/1748-9326/11/7/074029.

²⁴ Monkman and MacDonald, “On Carbon Dioxide Utilization as a Means to Improve the Sustainability of Ready-Mixed Concrete.”

²⁵ “Solidia Cement.”

²⁶ Claus Pade and Maria Guimaraes, “The CO₂ Uptake of Concrete in a 100 Year Perspective,” *Cement and Concrete Research* 37, no. 9 (September 1, 2007): 1348–56, doi:10.1016/j.cemconres.2007.06.009.

²⁷ Ibid.

²⁸ Monkman and MacDonald, “On Carbon Dioxide Utilization as a Means to Improve the Sustainability of Ready-Mixed Concrete.”

²⁹ Hsien H. Khoo and Reginald B.H. Tan, “Life Cycle Evaluation of CO₂ Recovery and Mineral Sequestration Alternatives,” *Environmental Progress* 25, no. 3 (October 1, 2006): 208–17, doi:10.1002/ep.10139; Hsien H. Khoo et al., “Carbon Capture and Mineralization in Singapore: Preliminary Environmental Impacts and Costs via LCA,” *Industrial & Engineering Chemistry Research* 50, no. 19 (October 5, 2011): 11350–57, doi:10.1021/ie200592h; Experience Nduagu, Joule Bergerson, and Ron Zevenhoven,

“Life Cycle Assessment of CO₂ Sequestration in Magnesium Silicate Rock – A Comparative Study,” *Energy Conversion and Management* 55 (March 2012): 116–26, doi:10.1016/j.enconman.2011.10.026; Abby Kirchofer et al., “Impact of Alkalinity Sources on the Life-Cycle Energy Efficiency of Mineral Carbonation Technologies,” *Energy & Environmental Science* 5, no. 9 (2012): 8631–41, doi:10.1039/C2EE22180B.

³⁰ Kirchofer et al., “Impact of Alkalinity Sources on the Life-Cycle Energy Efficiency of Mineral Carbonation Technologies.”

³¹ Nduagu, Bergerson, and Zevenhoven, “Life Cycle Assessment of CO₂ Sequestration in Magnesium Silicate Rock – A Comparative Study.”

³² Kirchofer et al., “Impact of Alkalinity Sources on the Life-Cycle Energy Efficiency of Mineral Carbonation Technologies.”

³³ Ibid.

³⁴ Scrivener, John, and Gartner, “Eco-Efficient Cements: Potential, Economically Viable Solutions for a Low-CO₂, Cement-based Materials Industry.”

Chapter 3: Commodity Chemicals

Today well over 350 Mt of organic chemicals—in the form of solvents, synthetic rubber, fiber, plastics and other products—are manufactured each year from fossil fuels.¹ Production of these organic chemicals results in approximately 2 GtCO₂ of CO₂ emissions from the direct and indirect use of fossil fuels.² Substitution of even a small fraction of this very large flow of materials and fuels represents an important opportunity for CO₂ utilization. While this large flow is composed of myriad products, the precursors to the finished products—i.e. commodity chemicals—are fewer and individually larger in production volumes (**Figure 3.1**).

Examples of these commodity chemicals include ethylene, propylene, methanol, butadiene and polyvinyl chloride. Typically, these chemicals have low profit margins, and thus use highly efficient production chains that are closely tied to petroleum

refining. Commodity chemicals, such as methanol, can also be finished products in themselves. As Figure 3.1 illustrates, there are many different direct and indirect routes by which CO₂ can be converted into a commodity chemical, some of which pass through synthesis gas (syngas).³

Commodity chemicals are one of the CO₂-based products considered in the roadmap because of the wide range of market opportunities, the possibility to scale up relatively mature technologies for commercial production in the medium-term, and the challenges in assessing the climate benefits of myriad production pathways and products. In this section, we review the technical challenges and R&D needs associated with the main conversion pathways, examine three example products, and look at issues in lifecycle assessment for commodity chemicals.

Technology and energy challenges

Carbon dioxide is a very stable, non-reactive molecule. As a gas (at standard temperatures and pressures) it has a lower energy than most other feedstocks used in industrial chemistry, meaning that it will not react to form other chemicals unless energy—often a substantial amount—is supplied to the process

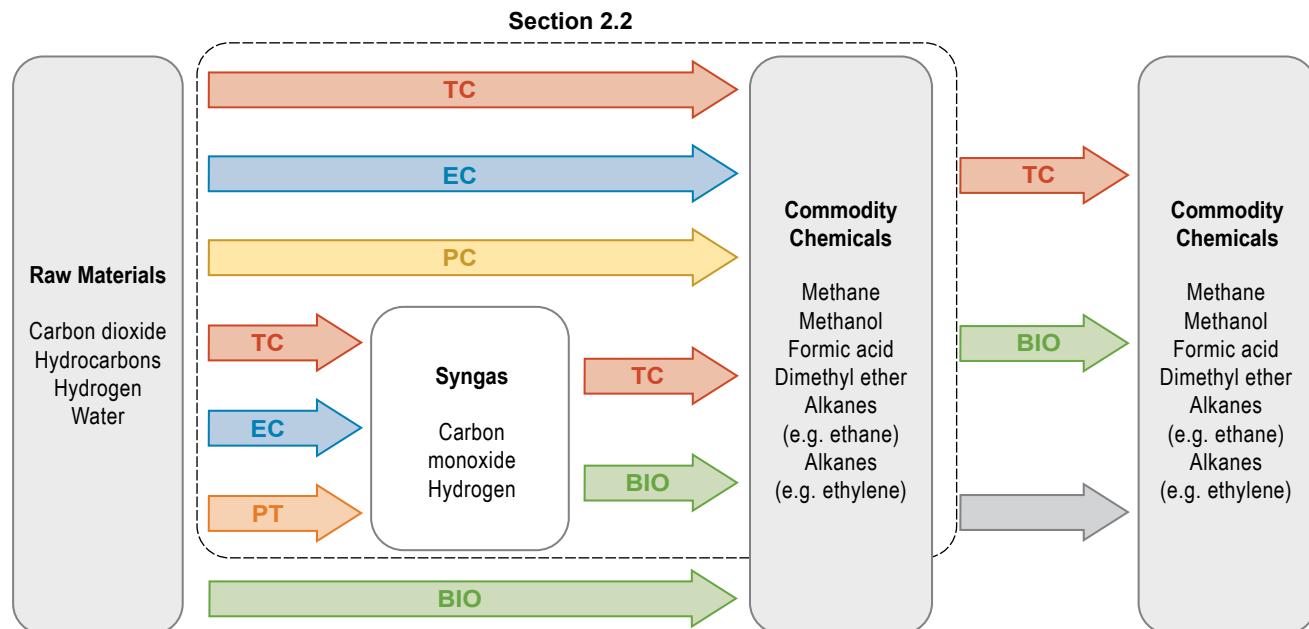


Figure 3.1. Direct and indirect routes (via synthetic gas, or syngas) for the conversion of raw materials to commodity chemicals, showing the multiple pathways that can be employed, linkages between commodity chemicals and finished products, and the scope of the chapter (in dashed lines). Pathway abbreviations are: thermocatalytic (TC), electrochemical (EC), photochemical (PC), photothermal (PT), and biological (Bio).

(Figure 3.2).⁴ This means that there are relatively few thermodynamically favorable reactions other than the carbonates discussed in Chapter 2 where CO₂ is a reactant, rather than a product. To use CO₂ as a reactant in the production of commodity chemicals generally requires energy to be added into the system, in the form of heat and electricity.

The amount of energy that must be added to create commodity chemicals from CO₂ depends on the change in the carbon atom's oxidation state. When CO₂ is incorporated into an organic molecule without a change in oxidation state (e.g. to make carboxylates, carbonates and carbamates), the amount of energy that must be added is small (see Figure 3.2).⁵ On the other hand, when CO₂ is chemically reduced through the addition of hydrogen (e.g. to make methanol or methane) the amount of energy that is added is quite large (in the form of process heat and the energy required to generate hydrogen). All other things being equal, synthesizing products from CO₂ that contain oxygen (e.g. aldehydes, carboxylic acids) requires significantly less energy than synthesizing hydrocarbons (e.g. alkanes, alkenes).

The fact that energy must be supplied for synthesis reactions involving CO₂ is not a problem, *per se*, as many common chemical processes, such thermal cracking of ethane to produce ethylene, require

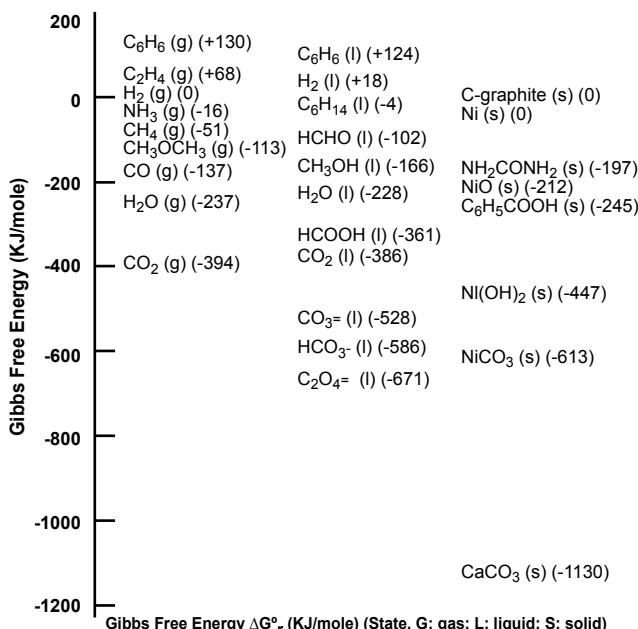


Figure 3.2. Free energy of formation for CO₂ and selected reaction products.⁶

external energy to be supplied.⁷ However, most of the energy required to drive these reactions typically comes from combustion of a portion of the fossil-based feedstock (or other fossil fuel) to provide heat.⁸ In CO₂ synthesis reactions, this energy must be provided from another source, which must have a relatively low-carbon intensity in order to provide an overall climate benefit (see “Example Pathways”).

As an example, Bennett et al. estimate that thermocatalytic production of ethylene from CO₂ and water (as a hydrogen source) would require a minimum input of 13.1 MWh of heat and electricity per ton of ethylene.⁹ Making all 32 Mt of ethylene produced in North America in 2016 from CO₂ would, thus, require over 423 TWh of electrical and thermal energy. If this use of CO₂ is to contribute to emissions reductions, the electricity and heat required would have to come from low-carbon sources. This would be the equivalent of consuming 1% of the total primary energy supply (TPES) for North America in 2016 or—more appropriately—about 5% of the total renewable and nuclear energy supply to make only ethylene.¹⁰

Multiple technology pathways exist for CO₂ conversion

Conversion pathways can be grouped into four broad categories:¹¹

- Thermocatalytic: where energy is provided in the form of heat (and pressure) and the reaction is facilitated by a catalyst;
- Electrochemical: where energy is provided in the form of electrons and products are generated in an electrochemical cell;¹²
- Biochemical: where living organisms or components thereof (e.g. enzymes) reduce CO₂ to products;
- Photochemical: where solar energy directly provides thermal or, via an intermediate material, electrical energy; and,
- Hybrid approaches: where pathways are combined (e.g. electrolysis coupled with Fisher-Tropsch synthesis, microbial electrolytic cells, solar-thermal conversions).¹³

The two primary thermocatalytic pathways are: direct hydrogenation of CO₂, and reduction of CO₂ to carbon monoxide followed by Fischer-Tropsch (F-T) or methanol synthesis (Figure 3.1). The chemistry of the direct hydrogenation route is generally well-known and

BOX 3.1 Commercial Methanol Production from CO₂

The first CO₂-to-methane facility, known as the George Olah Renewable Methane Plant, was designed, built and is operated by Carbon Recycling International (CRI) in Reykjanes, Iceland (see image below). It was commissioned in 2012 with a capacity of 1000 t/y of methanol (1.3 million liters) and was expanded to 4,000 t/y (5 million liters) in 2015.¹⁴ The CO₂ feedstock for the process is captured from a neighboring geothermal power plant, where it is a co-product of steam extraction for geothermal energy. Hydrogen is generated via electrolysis using low-carbon Icelandic grid electricity, and is used to directly hydrogenate the captured CO₂ to methanol using a heterogenous catalyst.¹⁵ The product, which CRI has branded “Vulcanol,” is then sold for use as a gasoline additive and as a feedstock for biodiesel production. The overall process has a low emissions footprint because of the extremely low emissions of the Icelandic grid; without this, the production of hydrogen for the process would likely result in very high overall emissions.



Image courtesy of CRI

has been commercialized for production of methane, methanol and dimethyl ether (in one step) from CO₂. Production of methanol from CO₂ has been tested at pilot scale by companies such as Mitsui and, today, a 5-million-liter-per-year CO₂-to-methanol plant is operating in Iceland (**Box 3.1**). Some view methanol as an excellent platform chemical for a CO₂-based economy, as efficient commercial processes exist to convert methanol to gasoline, olefins (e.g. ethylene, propylene), and dimethyl ether (in a two-step process).¹⁶ In practice, R&D challenges for direct hydrogenation include CO₂ activation, which requires better catalysts; and, low yields, which could be mitigated via more efficient separations.

Alternatively, F-T synthesis—that is, the conversion of carbon monoxide and hydrogen into hydrocarbons—is very well-known, having been discovered in the 1920s, commercialized during World War II, and used industrially today.¹⁷ Commercial F-T processes are commonly used to produce “syncrude,” which contains a wide range of hydrocarbons. The challenge for this route is reducing CO₂ to carbon monoxide, which is the feedstock for F-T synthesis. Options include the reverse water gas shift (RWGS) reaction, the forward version of which is used today in hydrogen production from fossil fuels; and, dry,¹⁸ bi-¹⁹ and tri-reforming²⁰ processes, which use methane (or other light hydrocarbons) to

reduce CO₂. Fundamental advances (e.g. lower-temperature catalysts, combining RWGS with separations) are required to commercialize RWGS and CO₂ reforming processes. In the case of CO₂ reforming, the use of fossil hydrocarbons means that it will be difficult to achieve significant emissions reductions relative to conventional synthesis from pathways in which this technology is employed—unless biomethane is used. Many other thermocatalytic options, such as chemical looping cycles, have also been proposed but are largely theoretical at this time.²¹

Most of the thermocatalytic pathways shown in **Figure 3.3** could involve an electrochemical step (i.e. electrolysis of water to generate hydrogen), making a hybrid process. In contrast, one-step electrochemical processes which convert CO₂ to commodity chemicals are rare. Laboratory and pilot-scale research has demonstrated the electrochemical reduction of CO₂ to, for example, formic acid using a range of metal electrodes (e.g. tin, indium, cadmium), methanol using ruthenium and titanium, methane using gold or copper, and ethylene using copper electrodes.²² In addition, the low-temperature electroreduction of CO₂ to CO (which differs from the SOEC route) has also been demonstrated, and could be a step in a hybrid electro-thermocatalytic process.²³ Startup companies

are active in this space,²⁴ but the technology has not yet reached the pilot stage.

Multiple challenges must be overcome in one-step electrochemical pathways, including: low faradic

efficiency,²⁵ particularly due to competing hydrogen evolution in aqueous solvent systems for strongly reduced products (e.g. methanol and methane); low current density, and hence production rates; and

BOX 3.2 Making the hydrogen needed to convert CO₂ to chemicals

Production of hydrogen—shown below in Figure 3.3—is a key step in both the direct and RWGS thermocatalytic routes for the conversion of CO₂ to chemicals, as well as in some electrochemical routes. Today, approximately 50 Mt of hydrogen are produced each year, over 95% of which is produced from fossil fuels, primarily through steam-methane reforming (SMR).²⁶ State-of-the-art SMR processes are highly efficient (>80% HHV), and generate a relatively high CO₂ concentration exhaust that is usually vented to the atmosphere. In principle, this CO₂ could be captured relatively easily and stored to reduce the carbon footprint of the produced hydrogen.²⁷ As of mid-2017 there are two operating SMR projects that capture and store CO₂: one in Canada²⁸ and another in the United States.²⁹

The remaining 4% of global hydrogen production comes from small-scale electrolysis³⁰ of water. Electrolysis is a proven process that is extremely efficient (>80% HHV) and can be carried out via alkaline electrolysis (AEL), proton exchange membrane (PEM), and solid oxide (SOEC) electrolysis. Both AEL and PEM electrolysis units are commercially available, and while AEL systems have a longer track record, PEM systems are more flexible and efficient.³¹ SOEC systems are still in the development stage but appear attractive for CO₂ conversion due to the possibility of co-electrolysis (direct production of syngas streams) and heat integration with F-T synthesis.³² In 2015, the International Energy Agency published a technology roadmap for hydrogen production (and fuel cells) that lays out goals and milestones for development of both electrolysis and production of hydrogen from fossil fuels with CCS.

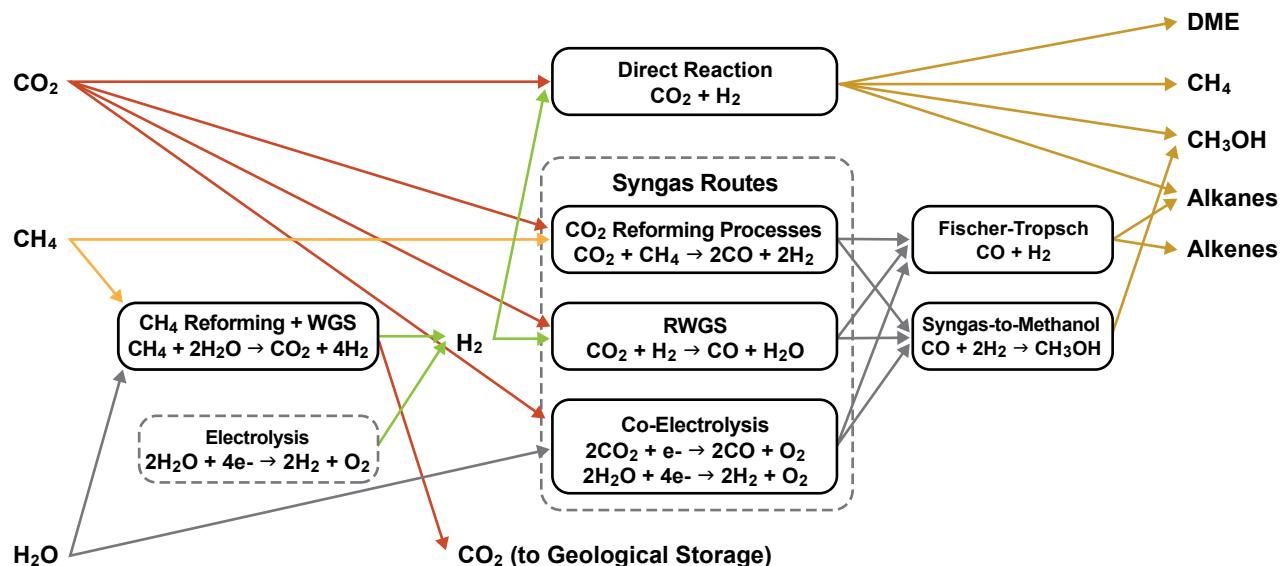


Figure 3.3. Selected thermocatalytic (and hybrid thermo-electrochemical) routes from CO₂ and water or methane to commodity chemicals.

poor stability of the electrodes. R&D in this space is needed to better understand the impacts of electrode structure on improving rates and stability, elucidate the fundamental relationships between the mechanisms of CO₂ reduction and electrode materials and structure, and develop improved design for practical applications (e.g. the use of gas diffusion electrodes to overcome mass transport limitations and reduce the separation costs associated with low yields).³³ One other promising area of active research relating to electrochemical pathways are “hybrid” microbial electrolysis cells, in which microbial communities living in the electrochemical cell reduce CO₂ to chemicals.³⁴

The predominant biological pathway for reduction of CO₂ to products is photosynthetic—the production of glucose from CO₂ in the presence of sunlight. Conversion of biomass to energy and materials has played a critical role in the development of society, and bioenergy crops—including algae—will likely play a larger role in the future as a means of addressing climate change.³⁵ While biomass pathways are not in the scope of this roadmap, non-photosynthetic biological pathways for the conversion of CO₂ directly to products are. These pathways use autotrophic organisms, which consume carbon monoxide, hydrogen, and CO₂ to generate reduced carbon molecules, such as ethanol or acetate.³⁶ At least one bioprocess that uses bacteria for the fermentation of synthesis gas streams to ethanol and butanediol has been demonstrated at the 300 t/y scale,³⁷ and larger facilities (on the order of 10,000 t/y) based on the process are in development.

An important benefit of biological pathways is that they operate under mild conditions and the organisms can be engineered to directly produce a range of organic chemicals that otherwise require multiple steps to produce from commodity intermediates (or cannot be synthesized industrially). Two notable drawbacks of such systems are that they usually require sterile conditions to avoid contamination and are difficult to hybridize with thermochemical pathways, the latter being the predominant means of producing syngas today.

The last standalone category is photochemical pathways, which come in two main types: thermal, where light is focused on a high-temperature reactor to reduce CO₂,³⁸ and catalytic, where a catalyst in solution or solid semiconductor absorbs light,

creating electrical energy which can reduce CO₂.³⁹ Photothermal pathways share much in common with the thermochemical pathways described above, with the additional complication that the process must be integrated with a solar collector and suffer the disadvantage of variable solar energy input. Photocatalytic pathways have been studied since the 1970s and, at the laboratory scale, have been shown capable of reducing CO₂ to formic acid, methanol, and methane. However, the efficiency and production rates of photocatalytic pathways remain too low to be commercially relevant, and don’t show a trend towards improvement (**Figure 3.4**).⁴⁰ A fundamental breakthrough is required if photocatalytic pathways are to become commercially relevant.

Consistent lifecycle assessments for CO₂ conversions remains a challenge

A robust life cycle assessment (LCA) framework is needed to determine whether a certain use of CO₂ can bring about a climate benefit – an overall reduction in emissions relative to an alternative, or even net negative emissions – and to quantify such benefits.⁴¹ The results of lifecycle assessments for commodity chemicals are important in several contexts. Results of LCA studies can help guide R&D expenditures towards products and processes that have the largest emissions reduction benefit and can be used to focus R&D on challenges that, if addressed, can have the largest possibility for improvement. They are also particularly important in informing decisions to incentivize (or invest in) production of a CO₂-based product and, if so, the appropriate level of the incentive. Finally, the environmental footprints of products can inform and influence consumer decision-making, even in the absence of policy.

In the LCAs performed to date, there are inconsistencies that make comparisons between various CCS and CO₂U options difficult,⁴² and the common pitfalls and limitations of LCA for organic chemicals have been comprehensively assessed elsewhere.⁴³ In summary, the main challenges in LCA for commodity chemicals are:

- The products of CO₂ utilization cannot easily be compared because they are not equivalent, nor are their uses. Thus, where comparisons are being made, the basis for comparison (i.e. the “functional unit”) must be chosen carefully. Moreover, the

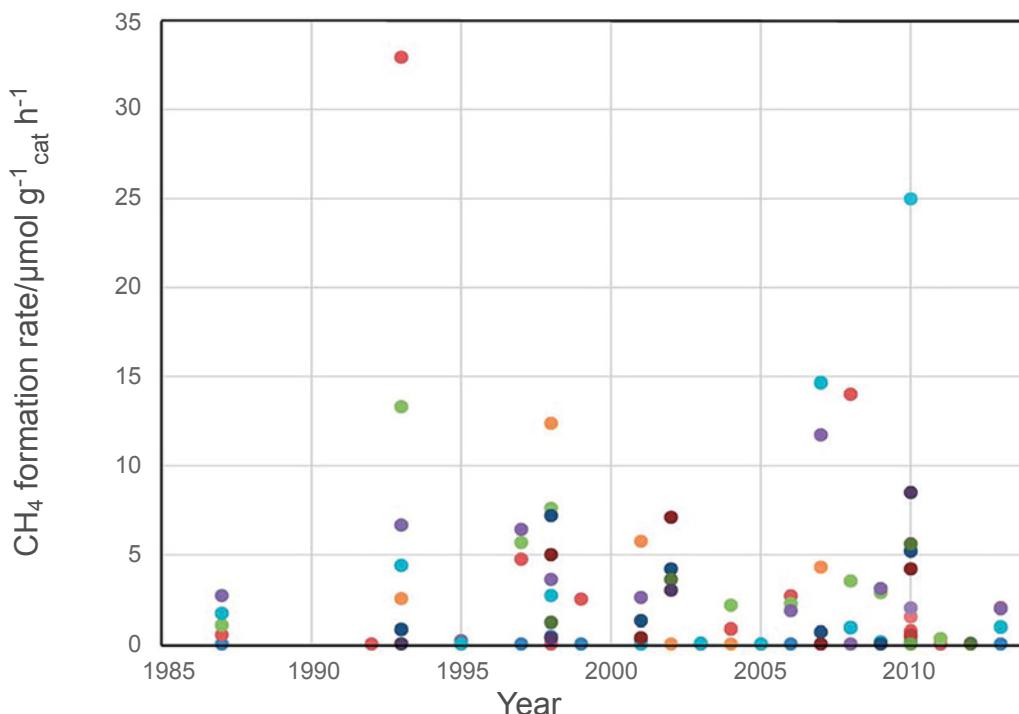


Figure 3.4. Rates of photocatalytic CO₂ conversion to methane reported in selected studies over time, as collected by Kondratenko et al.,⁴⁴ showing the limited progress that has been made to date in photocatalysis.

objective of the LCA may not always be served with a functional unit that is defined in terms of the product; rather, it could be in terms of an input such as units of CO₂⁴⁵ or hydrogen consumed.⁴⁶

- Commodity chemicals typically serve as feedstocks for other production processes that generate multiple finished products. Allocating the lifecycle emissions in multiple product systems such as these is not a new problem in LCA, but always a challenging one to solve.
- The products made from commodity chemicals are often used and disposed of in a range of different ways (e.g. reused, recycled, incinerated). Where products are long-lived or, at the end of life, disposed of in such a way that the carbon does not return to the atmosphere, they effectively sequester CO₂; conversely, assessing the climate benefits of products where CO₂ is temporarily sequestered is more difficult.⁴⁷ In theory, products that are long-lived and retain carbon over extended periods of time should have a benefit over those that are short-lived (e.g. fuels); however, LCA usually doesn't account for temporal distribution of impacts by convention (see Chapter 5 for a deeper discussion).
- The spatially varying carbon intensity of electricity and hydrogen inputs mean that results for

production in one region of the world cannot always be easily compared with another. For example, the grid electricity mix between neighboring countries dramatically impacts the emissions benefit of a range of single-carbon chemicals in Europe (**Figure 3.5**).⁴⁸

- The emission footprint of differing CO₂ feedstocks is variable and uncertain.⁴⁹ Although sources of high-concentration CO₂ are found in many chemical conversion facilities, most CO₂ sources are diluted and require concentration through separations. The environmental burdens associated with CO₂ capture may be substantial in comparison to those relating to CO₂ conversion (e.g. from an energy perspective, Kondratenko et al. present an example in which 60% of the total energy required to produce formic acid from CO₂ is due to CO₂ capture using amines).⁵⁰ In many cases, production chains do not result in net negative emissions, but an emissions benefit comes through the substitution of fossil-based products with lower carbon-intensity products. In such cases, the climate benefit of such displacements could be expected to decrease over time as climate policies “force out” the higher carbon-intensity products from the market.

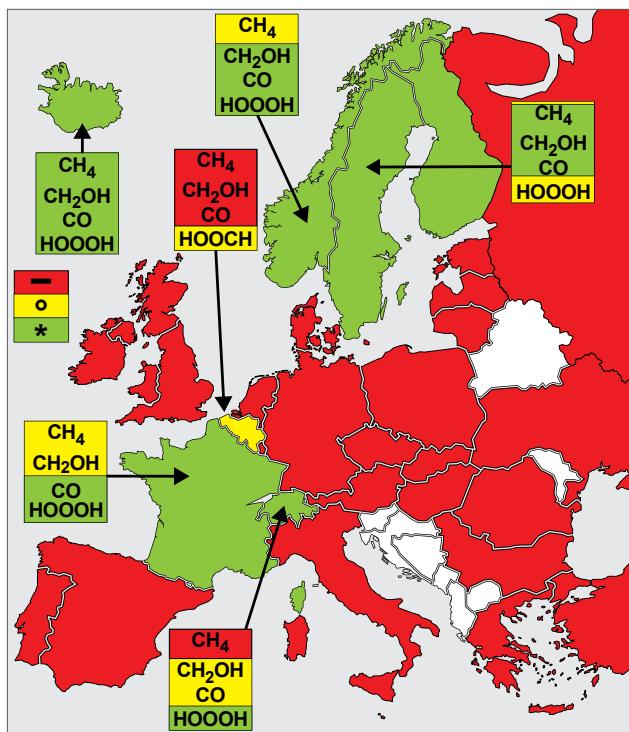


Figure 3.5. European countries where CO₂-based processes have the potential to achieve lower emissions impacts than fossil-based processes (in green and yellow) by using the national electricity mix of 2012 and an electrolysis unit with an efficiency of 50 kWh per kg H₂.⁵¹

Table 3.1. Example pathways across markets and TRL's.

| | | CO ₂ -Based Product | | |
|----------------------|---|--|-----------------------------|--------------------------|
| Market | Size (Mt/y) | Methanol | Formic Acid | Ethylene |
| | 100 (2020) ⁵³ | | | |
| Technology | Price (USD/t) | 70 (2015) 100 (2020) ⁵³ | 0.65 (2014) ⁵⁴ | 180 (2017) ⁵⁵ |
| | Pathway | Thermocatalytic (Direct hydrogenation) | Electrocatalytic | Electrocatalytic |
| | Development Stage (TRL) | Technology demonstration (6) | Laboratory pilot (3) | Laboratory studies (2) |
| Environmental Impact | Developers | CRI, Mitsui, Solvay | DNV, Mantra Energy, IFPEN | Opus12 |
| | Greenhouse Gas Emissions (MtCO ₂ /y) | 68-137 (avoided) ⁵⁶ | 1-3 (avoided) ⁵⁷ | Unknown |

In addition, it is important to recall that, while the focus of this discussion is on the use of LCA to assess climate benefits, the use of CO₂-based production pathways can also have wider environmental implications that should be considered. One prominent example is the production of dimethyl carbonate (DMC) via urea versus phosgene, in which the urea route—although not practiced industrially—was shown to have substantial benefits across a range of environmental impacts.⁵²

Example pathways

As the review in the preceding section illustrates, the number of possible combinations of technology pathways and products is very large. In this section, we describe three product pathways on the basis of markets, technologies and environmental impact. These pathways are described in **Table 3.1**.

The most advanced pathway is from CO₂ to methanol via direct hydrogenation of CO₂. While this is being undertaken commercially (as illustrated in Box 3.1), the largest facility is hundreds of times smaller than existing natural gas-based plants, which have capacities upwards of 5000 t/d. Thus, the technologies involved require further scale-up, by increasing

unit size, modular manufacturing capacity or some combination thereof. The economics of CO₂-based methanol production are difficult, however, as the estimated production cost is at least twice the current market price (even in an optimal case, where CO₂ is provided for free).⁵⁸ If current fossil-based methanol production was fully substituted for CO₂-based methanol—produced using electrolytic hydrogen and low-carbon electricity (i.e. approximately 50 gCO₂/kWh)—it would result in the avoidance of on the order of 100 MtCO₂/y.⁵⁹ This implies an avoidance cost of over \$800/tCO₂.⁶⁰

Both formic acid and ethylene production via electrolysis are at earlier stages of development, with the former having been tested at laboratory scale (i.e. kg/d) while the latter has only been observed in laboratory studies. Electrochemical production of formic acid using low-carbon electricity appears to be a promising option for emissions reduction; however, the small market size limits the cumulative emissions reduction to a few millions of tons per year.⁶¹ In contrast to methanol, the estimated production cost of formic acid is comparable to the current market price, and the avoidance cost is approximately \$30/t.⁶² Due to the very early stage of technology development, lifecycle and techno-economic assessments of the CO₂-based production of ethylene (via any route) have not yet been published.

Roadmap considerations

Given the wide range of potential products, multitude of pathways between CO₂ and any single product, and the wide range of development levels across pathways, it is unlikely that any single roadmap could cover the space. However, continued innovation in CO₂ conversion to commodity chemicals would benefit from development of roadmaps that target narrower groupings of products or technologies. **Figure 3.6** lays out an example of such milestones for catalysis advances and their relative sequence.

Key findings and recommendations

Findings

Conversion of CO₂ to commodity chemicals is daunting because of the energy-intensive nature of CO₂ reduction. However, not all products are equal in terms of their energy requirements: those where CO₂ is less deeply reduced (e.g. formic acid, formaldehyde, methanol) are relatively easier than alkanes (e.g. methane, ethane) or alkenes (e.g. ethylene). Demonstrated, commercially relevant thermocatalytic conversion pathways exist for production of methanol, dimethyl ether and methane from CO₂. However, these pathways require a low-carbon hydrogen source, either via reforming of fossil fuels with CCS or electrolysis of water using low-carbon electricity. Hybrid thermocatalytic pathways, such as co-reforming

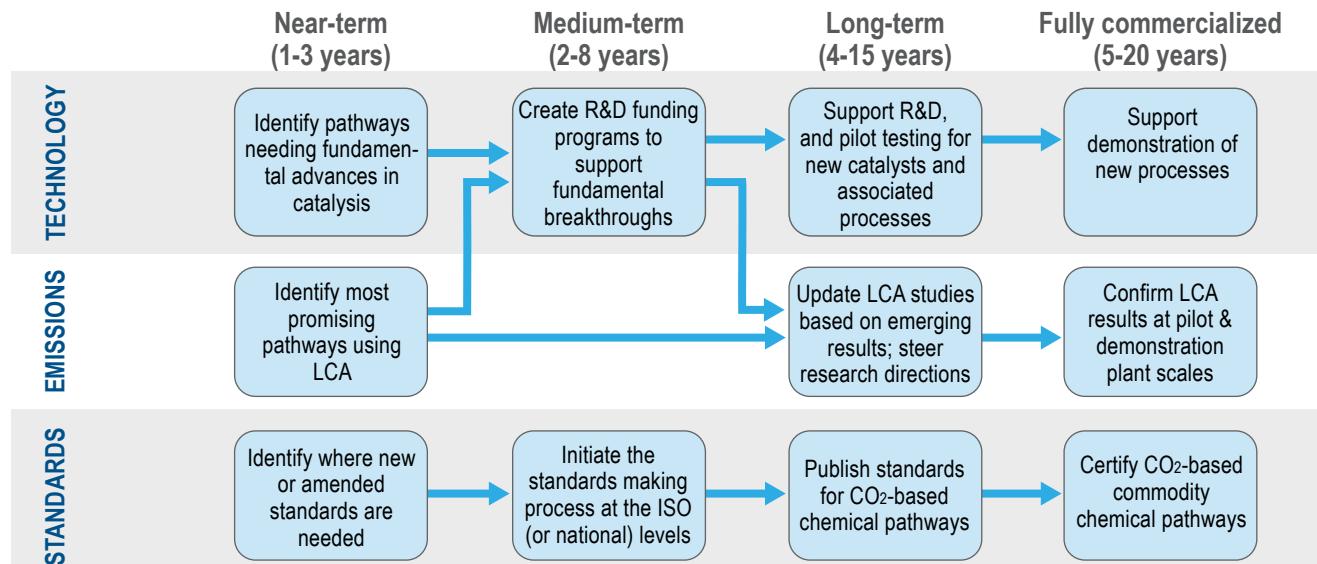


Figure 3.6. Conceptual roadmap for accelerating the innovation of CO₂ conversion to commodity chemicals.

using SOEC coupled with F-T or methanol synthesis, and fermentation of thermally (or electrochemically) produced syngas also appear promising.

Electrochemical reduction of CO₂ is a rapidly advancing field, and the production of carbon monoxide and formic acid seem to be relatively advanced compared to other products (e.g. methanol, methane, ethylene).

The climate benefit of producing commodity chemicals from CO₂ depends critically on the carbon intensity of the inputs—hydrogen, CO₂, heat, and electricity—which will vary depending on the production pathway and geographic location of the process. Commodity chemicals which have a greater potential to be used in durable products (as opposed to fuels) will have a larger benefit, as will those that displace carbon-intensive production pathways (e.g. methanol from coal).

Recommendations

Targeted R&D activities in the following areas would likely accelerate commercialization and improve performance for CO₂ conversion to industrial chemical feedstocks:

- Better catalysts would be inherently more efficient, and would reduce energy costs, improve yields, and improve emissions footprint. Rational design of catalysts (e.g. using computational DFT-based techniques) for thermo- and electrochemical pathways appear to be a priority.
- As renewable electricity becomes cheaper and provides a larger share of the grid electricity mix, electrochemical pathways become more attractive for the upgrading of CO₂. Modeling of CO₂ activation on metal surfaces for electrochemistry, innovations to improve electrode stability, and development of new cell designs are important targets for R&D.⁶³
- Advances in the fundamental understanding of high-temperature electrolysis (e.g. SOEC) are required, along with advances in materials to allow reliable, long-duration operation of SOEC cells.
- The combination of commercially available thermocatalytic pathways with emerging electro- or biochemical processes to create hybrid systems appears to be a promising strategy to advance CO₂ conversions⁶⁴ and modeling to evaluate the technical, economic and environmental performance is needed to drive innovation in this area. The combination of separations with reactions, long a

goal for chemical engineering research, would be particularly helpful to improve yields in all pathways.

- Innovative approaches are needed to advance photocatalysis and investments should focus on long-term R&D. In addition, practitioners should aim to make studies more consistent and comparable both in experimental design (e.g. light sources), but also in presentation of results (e.g. by providing better information on quantum yield or efficiency).⁶⁵
- There are few examples of life-cycle assessments for commodity chemicals today, and those that exist are difficult to compare. Additional studies are required to better define the potential climate (and environmental) benefit of the wide range of conversion pathways and products, and these studies should follow a consistent approach that improves their comparability.

Much remains to be understood regarding the chemical conversion approaches and life-cycle implications for a CO₂-to-chemicals enterprise. While some processes are near commercial, the possibilities to improve cost, performance, and emissions footprint are real. A coordinated innovation agenda in this space is a priority since many technical advances are new, many opportunities exist to improve, the technical readiness range is large, and the potential for climate benefits is high.

¹ D. Saygin et al., “Assessment of the Technical and Economic Potentials of Biomass Use for the Production of Steam, Chemicals and Polymers,” *Renewable and Sustainable Energy Reviews* 40 (December 2014): 1153–67, doi:10.1016/j.rser.2014.07.114.

² Total emissions from the “chemical” sector, excluding emissions from products used in agriculture as reported by: Bojana Bajželj, Julian M. Allwood, and Jonathan M. Cullen, “Designing Climate Change Mitigation Plans That Add Up,” *Environmental Science & Technology* 47, no. 14 (July 16, 2013): 8062–69, doi:10.1021/es400399h.

³ For the purpose of this discussion, we take a slightly different tack than the first version of the CO2U Roadmap in that we don’t treat syngas as a commodity chemical, but rather as an integral step in the production of commodity chemicals.

⁴ At low temperature and high pressure, carbon dioxide exists as a liquid, and has a higher energy than a small

number of industrially relevant chemicals. However, energy must be supplied to reach these temperatures and pressures, generally eliminating any energy advantage unless there is an opportunity to capture CO₂ directly from high pressure systems.

⁵ Michele Aresta, *Carbon Dioxide as Chemical Feedstock* (John Wiley & Sons, 2010).

⁶ Chunshan Song, "CO₂ Conversion and Utilization: An Overview," in *CO₂ Conversion and Utilization*, vol. 809, 0 vols., ACS Symposium Series 809 (American Chemical Society, 2002), 2–30, <http://dx.doi.org/10.1021/bk-2002-0809.ch001>.

⁷ Ibid.

⁸ U.S. DOE, "Manufacturing Energy and Carbon Footprint for Chemicals Sector (NAICS 325)," U.S. Department of Energy, 2014, <https://energy.gov/eere/amo/downloads/chemicals-2010-mecs>.

⁹ Bennett et al. consider two different pathways for ethylene production: generation of hydrogen from electrolysis followed by direct reaction and a second pathway corresponding to reverse water gas shift to produce CO followed by Fischer-Tropsch synthesis. Simon J. Bennett, David J. Schroeder, and Sean T. McCoy, "Towards a Framework for Discussing and Assessing CO₂ Utilisation in a Climate Context," *Energy Procedia*, 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12, 63 (January 1, 2014): 7976–92, doi:10.1016/j.egypro.2014.11.835.

¹⁰ IEA, "IEA - Statistics," International Energy Agency, accessed August 23, 2017, <https://www.iea.org/statistics/statisticssearch/>.

¹¹ M. Mikkelsen, M. Jorgensen, and F. C. Krebs, "The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide," *Energy & Environmental Science* 3, no. 1 (2010): 43–81, doi:10.1039/b912904a; Evgenii V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes," *Energy & Environmental Science* 6, no. 11 (2013): 3112–35, doi:10.1039/C3EE41272E.

¹² An electrochemical cell separates reduction, which occurs at the cathode, from oxidation reactions, which occur at the anode. Electrons travel through an external circuit connecting the anode and cathode (i.e. the electrodes), while ions travel through a semi-permeable membrane between the two "half-cells".

Because the products are evolved separately at the anode and cathode, no separations are required in an ideal process.

¹³ While not discussed here, other approaches show some promise. For example, see Ji-Jun Zou and Chang-Jun Liu, "Utilization of Carbon Dioxide through Nonthermal Plasma Approaches," in *Carbon Dioxide as Chemical Feedstock* (Wiley-VCH Verlag GmbH & Co. KGaA, 2010), 267–90, doi:10.1002/9783527629916.ch10.

¹⁴ CRI, "George Olah Plant," *Carbon Recycling International*, February 14, 2016, <http://carbonrecycling.is/georgeolah/>.

¹⁵ Olah, "Towards Oil Independence Through Renewable Methanol Chemistry."

¹⁶ George A. Olah, "Beyond Oil and Gas: The Methanol Economy," *Angewandte Chemie International Edition* 44, no. 18 (April 29, 2005): 2636–39, doi:10.1002/anie.200462121; George A. Olah, "Towards Oil Independence Through Renewable Methanol Chemistry," *Angewandte Chemie International Edition* 52, no. 1 (January 2, 2013): 104–7, doi:10.1002/anie.201204995.

¹⁷ Arno de Klerk, *Fischer-Tropsch Refining* (Weinheim: Wiley-VCH, 2011).

¹⁸ Devendra Pakhare and James Spivey, "A Review of Dry (CO₂) Reforming of Methane over Noble Metal Catalysts" 43, no. 22 (October 20, 2014): 7813–37, doi:10.1039/C3CS60395D.

¹⁹ George A. Olah et al., "Bi-Reforming of Methane from Any Source with Steam and Carbon Dioxide Exclusively to Metgas (CO–2H₂) for Methanol and Hydrocarbon Synthesis," *Journal of the American Chemical Society* 135, no. 2 (January 16, 2013): 648–50, doi:10.1021/ja311796n.

²⁰ Song, "CO₂ Conversion and Utilization."

²¹ Christopher Graves et al., "Sustainable Hydrocarbon Fuels by Recycling CO₂ and H₂O with Renewable or Nuclear Energy," *Renewable and Sustainable Energy Reviews* 15, no. 1 (January 1, 2011): 1–23, doi:10.1016/j.rser.2010.07.014.

²² Emily Barton Cole and Andrew B. Bocarsly, "Photochemical, Electrochemical, and Photoelectrochemical Reduction of Carbon Dioxide," in *Carbon Dioxide as Chemical Feedstock* (Wiley-VCH Verlag GmbH & Co. KGaA, 2010), 291–316, doi:10.1002/9783527629916.ch11; Jinli Qiao et al., "A Review of Catalysts for the Electroreduction of

Carbon Dioxide to Produce Low-Carbon Fuels," *Chemical Society Reviews* 43, no. 2 (2014): 631–75, doi:10.1039/C3CS60323G.

²³ Barton Cole and Bocarsly, "Photochemical, Electrochemical, and Photoelectrochemical Reduction of Carbon Dioxide."

²⁴ For example, Opus 12 (<https://www.opus-12.com/>)

²⁵ Faradaic efficiency is the ratio of the actual and theoretical amounts of a product formed based on charge passed. A 100% faradaic efficiency means that all of the electricity put into the system has gone into the production of that product.

²⁶ IEA, "Technology Roadmap: Hydrogen and Fuel Cells" (Paris, France: International Energy Agency, 2015), <https://www.iea.org/publications/freepublications/publication/technology-roadmap-hydrogen-and-fuelcells.html>.

²⁷ IEAGHG, "Techno-Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS" (IEA Greenhouse Gas R&D Program, 2017), http://ieaghg.org/exco_docs/2017-02.pdf.

²⁸ Shell, "CCS Facility Exceeding Expectations," Shell Canada, accessed August 25, 2017, http://www.shell.ca/en_ca/about-us/projects-and-sites/quest-carbon-capture-and-storage-project/carboncapture-and-storage.html.

²⁹ U.S. DOE, "Texas CO₂ Capture Demonstration Project Hits Three Million Metric Ton Milestone," U.S. Department of Energy, accessed August 25, 2017, <https://www.energy.gov/fe/articles/texas-co2-capture-demonstration-project-hits-three-million-metric-ton-milestone>.

³⁰ Manuel Götz et al., "Renewable Power-to-Gas: A Technological and Economic Review," *Renewable Energy* 85 (January 2016): 1371–90, doi:10.1016/j.renene.2015.07.066.

³¹ Gerda Gahleitner, "Hydrogen from Renewable Electricity: An International Review of Power-to-Gas Pilot Plants for Stationary Applications," *International Journal of Hydrogen Energy* 38, no. 5 (February 19, 2013): 2039–61, doi:10.1016/j.ijhydene.2012.12.010.

³² Graves et al., "Sustainable Hydrocarbon Fuels by Recycling CO₂ and H₂O with Renewable or Nuclear Energy"; Yun Zheng et al., "A Review of High Temperature Co-Electrolysis of H₂O and CO₂ to Produce Sustainable Fuels Using Solid Oxide Electrolysis Cells (SOECs): Advanced Materials and Technology," *Chemical Society Reviews* 46, no. 5 (2017): 1427–63, doi:10.1039/C6CS00403B.

³³ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes"; Qiao et al., "A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-Carbon Fuels."

³⁴ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes"; Heming Wang and Zhiyong Jason Ren, "A Comprehensive Review of Microbial Electrochemical Systems as a Platform Technology," *Biotechnology Advances* 31, no. 8 (December 1, 2013): 1796–1807, doi:10.1016/j.biotechadv.2013.10.001.

³⁵ Felix Creutzig et al., "Bioenergy and Climate Change Mitigation: An Assessment," *GCB Bioenergy* 7, no. 5 (September 1, 2015): 916–44, doi:10.1111/gcbb.12205.

³⁶ Ivan A. Berg et al., "Autotrophic Carbon Fixation in Biology: Pathways, Rules, and Speculations," in *Carbon Dioxide as Chemical Feedstock* (Wiley-VCH Verlag GmbH & Co. KGaA, 2010), 33–53, doi:10.1002/9783527629916.ch3.

³⁷ Derek W. Griffin and Michael A. Schultz, "Fuel and Chemical Products from Biomass Syngas: A Comparison of Gas Fermentation to Thermochemical Conversion Routes," *Environmental Progress & Sustainable Energy* 31, no. 2 (July 1, 2012): 219–24, doi:10.1002/ep.11613; LanzaTech, "Facilities," LanzaTech, accessed August 25, 2017, <http://www.lanzatech.com/facilities/>.

³⁸ Ee Teng Kho et al., "A Review on Photo-Thermal Catalytic Conversion of Carbon Dioxide," *Green Energy & Environment*, June 9, 2017, doi:10.1016/j.gee.2017.06.003.

³⁹ Barton Cole and Bocarsly, "Photochemical, Electrochemical, and Photoelectrochemical Reduction of Carbon Dioxide"; V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes."

⁴⁰ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes"; Mikkelsen, Jorgensen, and Krebs, "The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide."

⁴¹ Bennett, Schroeder, and McCoy, "Towards a Framework for Discussing and Assessing CO₂ Utilisation in a Climate Context."

⁴² Rosa M. Cuéllar-Franca and Adisa Azapagic, "Carbon Capture, Storage and Utilisation Technologies: A Critical Analysis and Comparison of Their Life Cycle Environmental Impacts," *Journal of CO₂ Utilization* 9 (March 2015): 82–102, doi:10.1016/j.jcou.2014.12.001.

⁴³ André Sternberg, Christian M. Jens, and André Bardow, "Life Cycle Assessment of CO₂-Based C1-Chemicals," *Green Chemistry* 19, no. 9 (May 8, 2017): 2244–59, doi:10.1039/C6GC02852G; Niklas von der Assen et al., "Selecting CO₂ Sources for CO₂ Utilization by Environmental-Merit-Order Curves," *Environmental Science & Technology* 50, no. 3 (February 2, 2016): 1093–1101, doi:10.1021/acs.est.5b03474; Niklas von der Assen, Johannes Jung, and André Bardow, "Life-Cycle Assessment of Carbon Dioxide Capture and Utilization: Avoiding the Pitfalls," *Energy & Environmental Science* 6, no. 9 (2013): 2721, doi:10.1039/c3ee41151f.

⁴⁴ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes."

⁴⁵ Cuéllar-Franca and Azapagic, "Carbon Capture, Storage and Utilisation Technologies."

⁴⁶ von der Assen et al., "Selecting CO₂ Sources for CO₂ Utilization by Environmental-Merit-Order Curves."

⁴⁷ Miguel Brandão et al., "Key Issues and Options in Accounting for Carbon Sequestration and Temporary Storage in Life Cycle Assessment and Carbon Footprinting," *The International Journal of Life Cycle Assessment* 18, no. 1 (June 2, 2012): 230–40, doi:10.1007/s11367-012-0451-6; Francesco Cherubini et al., "CO₂ Emissions from Biomass Combustion for Bioenergy: Atmospheric Decay and Contribution to Global Warming," *GCB Bioenergy* 3, no. 5 (October 1, 2011): 413–26, doi:10.1111/j.1757-1707.2011.01102.x; H. Herzog, K Calderia, and J. Reilly, "An Issue of Permanence: Assessing the Effectiveness of Temporary Carbon Storage," *Climatic Change* 59 (2003): 293–310.

⁴⁸ Sternberg, Jens, and Bardow, "Life Cycle Assessment of CO₂-Based C1-Chemicals."

⁴⁹ von der Assen, Jung, and Bardow, "Life-Cycle Assessment of Carbon Dioxide Capture and Utilization."

⁵⁰ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes."

⁵¹ Ibid.

⁵² Michele Aresta and Michele Galatola, "Life Cycle Analysis Applied to the Assessment of the Environmental Impact of Alternative Synthetic Processes. The Dimethylcarbonate Case: Part 1," *Journal of Cleaner Production* 7, no. 3 (March 1999): 181–93, doi:10.1016/S0959-6526(98)00074-2.

⁵³ Marc Alvardo, "The Changing Face of the Global Methanol Industry," *IHS Chemical Bulletin*, 2016.

⁵⁴ Ibid.

⁵⁵ Nandita Lal and James McKenna, "Will Europe's Bumper Steam Cracker Margins Be Sustained?," *Platts S&P Global*, accessed August 25, 2017, <https://www.platts.com/news-feature/2017/petrochemicals/global-ethyleneoutlook/europe-middle-east>.

⁵⁶ Guillaume Kerlero de Rosbo et al., "Valorisation Chimique Du CO₂: Etat Des Lieux – Quantification Des Bénéfices Énergétiques et Environnementaux et Évaluation Économique de Trois Voies Chimiques" (Angers, France: Agence de l'Environnement et de la Maîtrise de l'Energie, 2014), <http://www.ademe.fr/valorisation-chimique-co2-etatlieux- quantification-benefices-energetiques-environnementaux-evaluation-economique-trois-voies-chimiques>.

⁵⁷ Ibid.

⁵⁸ Kerlero de Rosbo et al., "Valorisation Chimique Du CO₂."

⁵⁹ Ibid.

⁶⁰ Ibid.

⁶¹ Kerlero de Rosbo et al., "Valorisation Chimique Du CO₂."

⁶² Ibid.

⁶³ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes."

⁶⁴ Gabriele Centi, Elsje Alessandra Quadrelli, and Siglinda Perathoner, "Catalysis for CO₂ Conversion: A Key Technology for Rapid Introduction of Renewable Energy in the Value Chain of Chemical Industries," *Energy & Environmental Science* 6, no. 6 (2013): 1711–31, doi:10.1039/C3EE00056G.

⁶⁵ V. Kondratenko et al., "Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes."

Chapter 4: Durable Carbon Materials

Introduction

The previous chapters examined CO₂U technologies that are near-to-market: already commercialized or technologically mature enough to be commercialized in the next decade. This chapter examines a CO₂U technology that is much farther from market, and is currently at the basic research stage: electrochemical methods to convert CO₂ directly into high-value solid carbon materials, such as carbon nanotubes, carbon fiber, graphene and diamonds (see **Box 4.1**).

There are two reasons to consider these far-from-market products in this roadmap. First, the market for these materials, particularly carbon fiber, is growing rapidly.¹ This is despite the fact that the current manufacturing technology is expensive, limiting commercial use to a small number of performance-sensitive applications (e.g. light-weighting aircraft for fuel savings). Lower-cost production methods would likely lead to even larger market growth. While it is too early to tell whether CO₂-based methods would result

in lower production costs, it is possible. This scenario is very different from the situation for cement and chemical intermediates, in which CO₂-based products will generally have to compete with conventional products in slower growing markets. Not surprisingly, entering a growing market is likely to be easier than competing with conventional incumbent products in a static market.

Second, this early-stage technology provides a case study of how policymakers can include emerging technologies that are still at the basic research stage in a comprehensive CO₂U strategy. The policy needs include funding support for basic research and development (R&D), some initial support for applied research and technology development, progressively detailed life-cycle emissions analyses (LCA), and early coordination with standards and certification bodies. This technology is not a good candidate for demand-creation policies such as tax incentives or mandates for buyers, unlike some of the technologies discussed earlier.

One concern that arises when discussing the carbon materials market is that the total mass of carbon that could be utilized is small, so the mitigation potential of CO₂-based durable carbon materials appears to be low. However, by some estimates it may be as high as 1% of global emissions (when potential growth

BOX 4.1 Pure carbon can exist in many different solid forms

The most well-known of these are **diamond** and **graphite**, which have both been used in commerce for centuries. More recently, other forms of solid carbon have been produced, whose properties depend strongly on their internal structure. **Graphene** is a single-layer hexagonal lattice of carbon atoms, and is an excellent electrical conductor as well as being one of the strongest materials known. **Carbon nanotubes** are seamless cylinders of graphene with diameters in the range of several nanometers; their strength and electrical properties have led to applications in batteries, automotive, electronics, sporting goods, and many other areas. **Carbon fiber** is a long, thin filament made primarily (although not entirely) of carbon atoms. These fibers are typically combined with a plastic resin to form a composite material known as carbon-fiber-reinforced polymer (CFRP, or sometimes just “carbon fiber”). This material has a wide range of applications for aerospace, automotives, energy, concrete reinforcement and sporting goods.



in market demand is included),² justifying serious consideration within a climate strategy. Also, because these materials are durable—unlike fuels and many chemicals—they will not rapidly return carbon dioxide to the atmosphere, making them very attractive from a life-cycle point of view.

A key aspect of these high-value products is that the economic value generated by producing them from CO₂ could help spur additional privately funded research and investment in CO₂ capture and conversion technologies. If so, the overall climate impact of the introduction of CO₂-based durable carbon materials will be larger than their primary emissions mitigation.

State of the technology

Research beginning in the 1960s revealed that it was possible to deposit solid carbon using electrolysis in molten salts that contain lithium and carbonate ions (CO₃²⁻).³ The deposited carbon was either poorly characterized or found to be mostly amorphous, and therefore not particularly interesting economically or technologically. More recently, researchers began to consider the possibility of using this process to capture and convert CO₂. The main electrochemical process first reduces carbonate ions in the melt, which then produces both solid carbon and oxide ions. These oxide ions next react with CO₂ to form more carbonate ions, resulting in a net conversion of CO₂ to solid carbon.⁴ While the precise chemistry remains imperfectly understood, a growing number of studies have demonstrated the process (see **Table 4.1**). These experiments typically use molten lithium carbonate (Li₂CO₃) or Li-Na-K carbonate mixtures as an electrolyte, with temperatures in the range of 500-700 °C. The electrolyte is not consumed in the reaction; instead, CO₂ from the air (generally unpressurized) is consumed, and solid carbon is deposited on one electrode. In parallel to the work with molten carbonates, researchers have also explored electrolysis using molten salts such as CaCl₂, NaCl, and KCl, or combinations of carbonates and molten salts, at similar temperatures.

More recently, researchers have improved their ability to characterize the deposited carbon and begun to modify the process conditions to be able to produce complex, nanostructured carbon materials. These materials—particularly carbon nanotubes,

carbon fibers and graphene—are extremely valuable commercially, far more than amorphous carbon. This development has brought renewed attention to the field, because it suggests that a technology based on this process could simultaneously capture CO₂ and produce highly economically valuable materials.

While encouraging, these results have only been reported by a small number of research groups (in some cases, a single group) and have only achieved a total production scale of less than a kilogram of material. They therefore need to be considered with caution, and the main results must be reproduced by other researchers, both to validate them and to broaden the understanding of the underlying methods across the research community. The methods are well-described in the published literature, so replicating them should be relatively straightforward.

Table 4.1. Representative reported results of durable carbon materials produced from CO₂.

| Representative studies | Products reported |
|--|-------------------------------------|
| Licht (2016) ⁵ ; Wu (2016) ⁶ ; Johnson (2017) ⁷ | Carbon nanotubes, carbon nanofibers |
| Douglas (2017) ⁸ | Carbon nanotubes |
| Yin (2013) ⁹ | Carbon powder |
| Le Van (2009) ¹⁰ | Carbon powder |
| Tang (2013) ¹¹ | Carbon powder, carbon nanosheets |
| Hu (2016) ¹² | Graphene |
| Kamali (2017) ¹³ | Nano-diamonds |
| Hu (2017) ¹⁴ | Carbon nanotubes |
| Novoselova (2007) ¹⁵ | Carbon nanotubes, carbon nanofibers |

There is currently very limited effort to commercialize this process; one early-stage U.S.-based company is using molten carbonate electrolysis to produce graphite.¹⁶

Beyond the need for replicating and validating these results, the other important research pathways include:

- **Production quality:** Improving the understanding of the process conditions for forming various types of carbon materials, with a particular focus on controlled morphologies of carbon nanotubes, is essential. This is an active area of research, and

includes both increasing the yield of valuable materials and controlling their uniformity.¹⁷

- **Alternatives to lithium:** Investigating alternative carbonate electrolytes and mixtures will be needed. Much of the current research has focused on lithium carbonate or the ternary mixture Li-K-Na carbonate.¹⁸ Lithium carbonate is in high demand globally by lithium battery manufacturers, and doubled in price from 2016 to 2017.¹⁹ The price may continue to increase as the demand for lithium ion batteries grows. Minimizing the necessary amount of lithium carbonate for electrolytic carbon material production will likely be important for controlling costs. In the long term, global production of lithium carbonate should respond to rising demand and prices should stabilize, meaning that these cost concerns may eventually fade.
- **Production scale-up:** Scaling production above kilogram quantities is required, including developing pilot-scale electrolysis facilities that can demonstrate higher material throughput. This will take substantial applied engineering research, including developing technology for high-temperature electrolysis at scale and developing concepts for how to enhance the production cycle (for example, creating continuous production instead of batch production). This kind of R&D is often difficult for policy makers and sponsors to support, and may need targeted policy support. It is important to note that there are strong technical synergies with molten carbonate fuel cells, which

are commercialized and operate at multi-megawatt scale²⁰ (see **Box 4.2**).

- **LCA-guided R&D:** As discussed below, a full life cycle analysis is not yet possible, given the early stage of the technology. However, basic insights are possible, such as identifying the most likely sources of life cycle emissions in the processes being researched. This can be used to guide the most important directions for research.²¹ However, research groups that are concerned with achieving basic technical results are often not equipped or funded to also conduct LCAs, even at a basic level, so funding agencies should explicitly include support for this, or work to connect research groups with LCA researchers who can provide the necessary expertise.

Market and utilization considerations

If these research challenges can be met, producing durable carbon materials will become particularly interesting from a CO₂U point of view, for several reasons.

First, the (very) **high value of these materials**, particularly carbon nanotubes, creates a powerful economic motivation for the private sector to develop and deploy the technology, once it reaches a certain stage of technological maturity in the laboratory. This is very different from lower-value CO₂-based products such as cement and some industrial chemicals, whose low market value implies that long-term policy

BOX 4.2 Molten Carbonate Fuel Cells

Molten carbonate fuel cells (MCFC) are stationary power systems that convert a variety of fuels (primarily natural gas) into electricity and heat. They consist of a carbonate-based electrolyte (usually a mixture of lithium, potassium and/or sodium carbonate) and nickel-based electrodes, and operate at approximately 650° C. MCFCs are currently being piloted for carbon capture at coal-fired power plants, because they require CO₂ for operation and may be able to significantly reduce the costs of capturing and concentrating CO₂ compared to conventional amine-based processes.²² MCFCs are also used in cogeneration applications, and even tri-generation (production of power, heat, and hydrogen).²³ Operating MCFCs in “reverse” mode as an electrolysis cell is an active area of research.²⁴



support (such as a carbon price) will be needed to drive deployment well after the technology is mature. This means that although public funding for R&D is necessary at this early stage of the research, longer-term public funding will not likely be necessary. Therefore, public investments in early-stage R&D to develop CO₂-based durable carbon materials production are likely to have high payoffs, without creating a need for long-term policy support.

Second, these materials are very **long-lived**, and don't return CO₂ to the atmosphere quickly. This is in stark contrast to CO₂-based fuels and chemicals, many of which are burned or otherwise processed within days or weeks, releasing their stored carbon dioxide. In fact, carbon fiber composites in particular are so durable that they don't break down in landfills, a fact that has caused concern about solid-waste accumulation and led to support for R&D on recovery and recycling.²⁵ While carbon fiber recycling technology will probably be developed, the rapid growth in demand for carbon fiber means that recycling alone will never provide sufficient supply. An analogous case can be made for synthetic diamonds, where production breakthroughs could increase the use of diamonds in other applications (e.g. diamond-based quantum computing).²⁶ Ultimately, a process that locks atmospheric CO₂ into an immutable solid carbon form that is landfilled is likely to compare favorably with any short-lived carbon product from a climate point of view.

Third, many of the applications of carbon materials, particularly carbon nanotubes, carbon fiber, and graphene, have **ancillary emissions reductions benefits**. Some examples of this include improving aircraft and vehicle fuel efficiency through light-weighting with carbon fiber, enhancing wind turbine blade performance with carbon fiber²⁷ and graphene,²⁸ enabling lightweight hydrogen and natural gas storage tanks for vehicles with carbon fiber, improving vehicle fuel efficiency using polycarbonate windows, and improving the capacity of lithium ion batteries with graphene electrodes²⁹ (which could accelerate the adoption of electric vehicles). This is in stark contrast with the case of CO₂ utilization for enhanced oil recovery (EOR), where the storage of captured CO₂ is offset by emissions from the produced oil.

If carbon materials could be manufactured at lower cost than with conventional technology, they could

penetrate other important markets where they are not currently competitive, including electronics, sensors and optics. There may be an opportunity to develop carbon-fiber-based shipping containers, which would be significantly lighter than aluminum, resulting in fuel savings, and possibly ancillary benefits such as more rapid security inspections.³⁰ Carbon fiber composites re-entering architectural use as structural elements (often replacing steel rebar) and as seismic retrofits for reinforced concrete.^{31,32} Lower-cost carbon fiber could compete more extensively with steel in concrete reinforcement applications, and could also prolong the life of concrete structures through carbon-fiber fabric wrapping and lightweight structural reinforcements. Finally, there has been initial research on the use of carbon fiber additives to reinforce asphalt (improving lifetime and reducing the need for repaving) and to make asphalt electrically conductive as a runway de-icing strategy.³³

Within this broad range of materials, the largest market potential, both in terms of value and total mass flow, is carbon fiber. Average costs of carbon fiber vary by application (reflecting different quality) and range from \$28/kg to \$116/kg, while the overall market is growing at 12.5% CAGR.³⁴ A key issue in the carbon fiber market is the fact that there is a small number of major manufacturers globally, all of whom use proprietary and non-standard production processes. This, combined with the fact that there are significant new non-conventional carbon fiber production methods being introduced to the market (notably lignin precursors)³⁵ means that any CO₂-based carbon fiber materials will face complex and potentially unclear product specifications and standards in order to enter the market. While resolving this complication is outside the scope of CO₂U policy (and this roadmap), the situation should be monitored as CO₂-based carbon material production moves toward the applied research stage.

As with cements, aggregates, chemicals, and fuels, long-lived CO₂-based materials must achieve certain performance standards and receive approval and certification to enter the market. Because the approaches discussed here are relatively exotic, CO₂-based materials face additional hurdles in permitting and standardization. These hurdles can, in part, be addressed by crafting performance-based regulations and standards—something already encouraged by

most standardization bodies, but still uncommon in practice. Nonetheless, it is likely that standards-setting organizations and procurement organizations are currently mostly unfamiliar with the idea of CO₂-based substitute materials, their manufacturing approaches, and issues of quality and defect occurrence. Therefore, there is a potentially important role from a policy perspective in jump-starting the education and evaluation process of these technologies within key organizations in order to avoid regulatory or statutory delays in new CO₂-based products entering markets. Key organizations for this include the International Organization for Standardization (ISO), ASTM International, and the International Electrotechnical Commission (IEC).

Life cycle analysis considerations

Life cycle analysis (LCA) of the very early-stage CO₂-based carbon materials technologies described here is probably premature. However, there are several issues that will clearly impact any future LCA when the technology is more advanced. The first is the energy source used in the conversion process, which is relevant for some processes (e.g. high-temperature electrolysis or diamond crystallization). The carbon intensity of the electricity used will strongly impact the overall LCA; at industrial scale this may simply be determined by the local power grid, but could potentially directly incorporate solar or other renewable electricity sources.³⁶

A second issue will be the thermal efficiency of the (likely high-temperature) process, including heat recovery. As a point of comparison, in commercial aluminum smelting, roughly half the input energy is lost as waste heat, with significant unexploited opportunities to better capture it.³⁷ Heat management will clearly be determined in part by process engineering, and should be included at an early stage in the design considerations. Notably, in the Hall-Héroult process, produced aluminum is periodically siphoned from the cell in liquid form, meaning that cells can operate continuously without having to be cooled and re-heated. It may be necessary to develop some analogous method for recovering produced carbon materials continuously rather than temperature-cycling the cells (thereby dramatically improving both efficiency and productivity).

The third issue that can be anticipated at this stage is the emissions footprint of any consumed electrode or electrolyte materials, or other reactants. Until the process details can be developed and better understood through further early-stage research, it is difficult to make any predictions about this. The best approach would be to include ongoing attention to the emissions consequences of these materials/reactants in the core research stream (also known as LCA-guided design).

Any LCA of CO₂-based carbon materials production should be compared with conventional production routes, and alternative production methods under consideration. This should specifically include a comparison with recovery and recycling of carbon fiber composites (where the embedded energy savings may be quite large) and carbon fiber production methods using non-petroleum-based precursor feedstock.³⁸

Roadmap considerations

Given the very early-stage nature of this technology, it is not possible to develop a roadmap that includes a detailed industrial scale-up strategy. But within the constraints of the current technology maturity, there are clear milestones for advancing the core technology (including manufacturing), the understanding of overall emissions, and market acceptance of CO₂-based carbon materials through standards and certification. Figure 4.1 lays out these milestones and their relative sequence.

Key findings and recommendations

Findings:

- Early-stage research has shown that there are pathways for converting CO₂ directly into a range of durable carbon materials.
- Some of these materials, particularly carbon fiber, have large and valuable potential markets.
- The long-lived nature of these products, and their ancillary emissions benefits (such as improving fuel efficiency through vehicle light-weighting) imply that the life-cycle emissions impacts will be favorable.
- Currently, there is a need for increased early-stage R&D support to replicate results and improve the core technology.

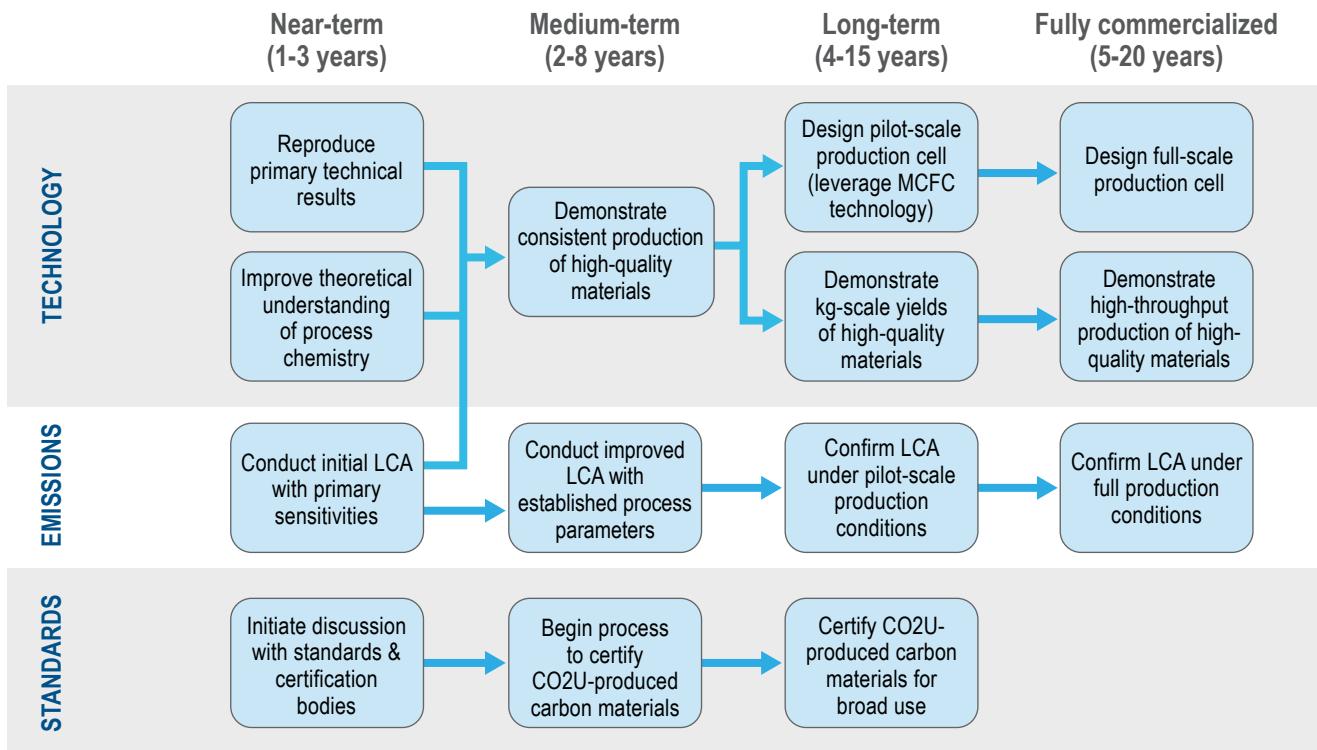


Figure 4.1. Conceptual roadmap for accelerating the development and commercialization of CO₂-based durable carbon materials.

- Applied research support for scaling up production from the laboratory scale will be necessary in the medium term. This should be accompanied by life cycle emissions analyses that progressively refine their estimates as the technology matures.
- There are technology synergies with molten carbonate fuel cells, and that research community should be encouraged to partner with research efforts on CO₂-based durable carbon materials.

It is too early to consider market-pull policies such as subsidies or purchase mandates for these technologies. Also, the fact that many of these carbon materials would enter markets in which there is already significant demand means that market-pull policies may not be necessary at all in the future.

Recommendations:

- Decision-makers should increase investment in conversion of CO₂ to long-lived, high-value carbon-based products, and support long-term, stable research programs to improve the chances of successful outcomes.
- New LCA data and methods are needed to better understand the climate benefits of these processes

and materials. R&D programs should incorporate life cycle considerations into planning to maximize the likely climate benefits of the resulting technologies.

- Governments and companies should engage early with standards-setting organizations in order to avoid delays in market introduction of these products. The key focus should be on education, process discussions, and regulatory concerns.

¹ S. Das et al, “Global Carbon Fiber Composites Supply Chain Competitiveness Analysis”, Clean Energy Manufacturing Analysis Center, ORNL/SR-2016/100 | NREL/TP-6A50-66071 (2016).

² Douglas and Pint, “Review – Electrochemical Growth of Carbon Nanotubes and Graphene from Ambient Carbon Dioxide: Synergies with Conventional Gas-Phase Growth Mechanisms”, ECS J. S. S. Sci. & Tech. (2017).

³ Ingram et al, “The electrolytic deposition of carbon from fused carbonates”, Electrochimica Acta (1966).

⁴ Ijije and Chen, “Electrochemical manufacturing of nanocarbons from carbon dioxide in molten alkali metal carbonate salts: roles of alkali metal cations”, Advances in Manufacturing (2016).

⁵ Licht et al, "Carbon Nanotubes Produced from Ambient Carbon Dioxide for Environmentally Sustainable Lithium-Ion and Sodium-Ion Battery Anodes", *ACS Central Science* (2016).

⁶ Wu et al, "One-pot synthesis of nanostructured carbon materials from carbon dioxide via electrolysis in molten carbonate salts", *Carbon* (2016).

⁷ Johnson et al, "Carbon nanotube wools made directly from CO₂ by molten electrolysis: Value driven pathways to carbon dioxide greenhouse gas mitigation", *Materials Today Energy* (2017).

⁸ Douglas et al, "Sustainable Capture and Conversion of Carbon Dioxide into Valuable Multiwalled Carbon Nanotubes Using Metal Scrap Materials", *ACS Sus. Chem. & Eng.* (2017).

⁹ Yin et al, "Capture and electrochemical conversion of CO₂ to value-added carbon and oxygen by molten salt electrolysis", *E&E Science* (2013).

¹⁰ Le Van et al, "Electrochemical formation of carbon nano-powders with various porosities in molten alkali carbonates", *Electrochimica Acta* (2009).

¹¹ Tang et al, "Effects of applied voltage and temperature on the electrochemical production of carbon powders from CO₂ in molten salt with an inert anode", *Electrochimica Acta* (2013).

¹² Hu et al, "Direct Conversion of Greenhouse Gas CO₂ into Graphene via Molten Salts Electrolysis", *ChemSusChem* (2016).

¹³ Kamali, "Nanocatalytic conversion of CO₂ into nanodiamonds", *Carbon* (2017).

¹⁴ Hu et al, "Electrochemical deposition of carbon nanotubes from CO₂ in CaCl₂-NaCl-based melts", *J. Mat. Chem. A* (2017).

¹⁵ Novoselova et al, "Electrolytic production of carbon nano-tubes in chloride-oxide melts under carbon dioxide pressure", *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials* (2007).

¹⁶ See "Advanced Manufacturing for Low-cost High-performance graphite", US Department of Energy website; "SBIR Phase I: Supercritical Carbon Dioxide Assisted Purification of Electrolytically Synthesized Graphite", SBIR website.

¹⁷ Ren et al, "Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection of carbon nanotubes", *Journal of CO₂ Utilization* (2017).

¹⁸ Ijijie et al, "Carbon electrodeposition in molten salts: electrode reactions and applications", *RSC Advances* (2014).

¹⁹ McCormick, "Lithium contract prices for 2017 double 2016 levels", *Industrial Minerals* (2016).

²⁰ McPhail et al, "International status of molten carbonate fuel cells technology", *IEA Energy Technology Network* (2015).

²¹ Holman et al, "Using Life Cycle Assessment to Guide Catalysis Research", *Ind. Eng. Chem. Res.* (2009).

²² "Fuel Cell Energy and Exxon Mobil Announce Location for Fuel Cell Carbon Capture Pilot Plant", *Fuel Cell Energy* press release (2016).

²³ Rinaldi et al, "Study of CO₂ recovery in a carbonate fuel cell tri-generation plant", *J. Power Sources* (2015).

²⁴ Hu et al, "Performance and Durability of the Molten Carbonate Electrolysis Cell and the Reversible Molten Carbonate Fuel Cell", *J. Phys. Chem. C* (2016).

²⁵ Barnes, "Recycled carbon fiber: Its time has come", *Composites World* (2016).

²⁶ Nemoto et al, "Photonic Architecture for Scalable Quantum Information Processing in Diamond", *Phys. Rev. X* (2014).

²⁷ "Wind energy blowing life into global carbon fiber industry", *Windpower Engineering & Development* (2013).

²⁸ "Graphene-reinforced composites may lead to longer, lighter blades and more", *Windpower Engineering & Development* (2014).

²⁹ Zhu et al, "The application of graphene in lithium ion battery electrode materials", *Springerplus* (2014).

³⁰ "Composites could revolutionize shipping containers", *Plastics Today* (2014).

³¹ "Carbon fiber grids replace steel as innovative concrete reinforcement", *JEC Group* (2013).

³² Sara Black, "Carbon fiber: Key to cost-conscious rehab", *High-Performance Composites* (2014).

³³ "Fiber Additives in Asphalt Mix", *Transportation Research Board* (2015).

³⁴ Das, op. cit.

³⁵ Sara Black, "Alternative precursor R&D: Lignin in the lightweighting limelight", *Composites World* (2016).

³⁶ Licht et al, "A New Solar Carbon Capture Process: Solar Thermal Electrochemical Photo (STEP) Carbon Capture", *J. Phys. Chem. Lett.* (2010).

³⁷ Nowicki and Gosselin, "An Overview of Opportunities for Waste Heat Recovery and Thermal Integration in the Primary Aluminum Industry", *JOM* (2012).

³⁸ Mainka et al, "Lignin – an alternative precursor for sustainable and cost-effective automotive carbon fiber", *J. Mat. Res. Tech.* (2015)

Chapter 5:

Life Cycle Assessment

Estimating the emissions reduction benefit

Most of the recent interest in CO₂ utilization has been driven by the goal of stabilizing greenhouse gas (GHG) concentrations in the atmosphere (Chapter 1). As this roadmap highlights, CO₂-based products vary widely in the amount of CO₂ they incorporate, the energy intensity of their production, the markets in which they compete, and their lifetime and ultimate disposal. Determining the climate benefit of a CO₂-based product depends on these and other factors.

Consider the process of converting CO₂ to methanol, using hydrogen generated from water electrolysis as an example. The climate impacts of that process will depend on several factors: the emissions associated with capturing and transporting the CO₂ used as a feedstock, generating the electricity used in production, and the emissions avoided by displacing manufacture of methanol made from fossil fuels, amongst others. According to one recent study, displacement of fossil fuel-based methanol is a particularly crucial factor.¹ Thus, looking at the GHG emissions associated with only the production of CO₂-based methanol presents a partial—and potentially misleading—picture of its emissions impact.

Assessing the capacity of the myriad CO₂-based products and conversion pathways to contribute to stabilization of GHG concentrations requires

systems thinking. This includes an understanding of the multiple steps involved in product manufacture; flows of energy, materials, and waste between them; and, the sources of raw materials and the final uses of products. Life cycle assessment is a structured method of assessing the environmental sustainability of a system. Although assessing the emissions reduction potential of CO₂ utilization (CO2U) poses methodological challenges, life cycle assessment is well-suited to the task.

What is life cycle assessment and why does it matter?

Life cycle assessment (LCA) quantifies inputs (including materials and energy) and outputs (including wastes) over the life cycle of a process or product—ideally from “cradle-to-grave”—and then assesses their impacts to human health and the environment. The general principles, framework and requirements for LCA are widely accepted and have been codified in ISO standards,² with additional guidance provided by organizations such as the European Commission³ and U.S. Environmental Protection Agency.⁴ Many energy and environmental policies have been developed with life cycle thinking in mind; indeed, a growing number of laws and regulations require the use of LCA. Notable examples include the European Union’s Waste Framework Directive,⁵ Fuel Quality Directive (FQD),⁶ and Renewable Energy Directive (RED).⁷ Examples in the United States include the Renewable Fuel Standard (RFS); and the California Low Carbon Fuel Standard (LCFS).⁸

The ISO LCA standards provide for a great deal of flexibility in their application and have been applied to a wide range of processes and products. An LCA compliant with the ISO Standard will have a clearly



defined goal and scope, inventory analysis, impact assessment and interpretation of the results. The goal and scope will include a statement of the intended application for the results, the rationale for undertaking the work, a clear delineation of the boundaries of the system, and the “functional unit” for the analysis (e.g. a MWh of electricity, ton of formic acid, or kilometer traveled). Whether the boundaries of an LCA truly encompass the entire life cycle—from the production of raw materials through to disposal of the products—depends on the goals and intended application for the LCA. For example, where the objective is to compare a CO₂-based product with an identical product on the market (e.g. methanol), the use and final disposal of the products are the same and consideration of the entire lifecycle may not be needed.⁹

During the inventory analysis, the inputs and outputs are estimated for each part of the process in question and then summed to provide system-level results. The results of the inventory analysis are mass, volumetric or energy flows normalized to the functional unit of the LCA (e.g. kg of CO₂, m³ of water or MJ of oil per unit product). These inventory analysis results are sometimes presented as the end results, in which case the study should be properly referred to as a life cycle inventory (LCI). In the life cycle impact assessment (LCIA), the inventory analysis results are then translated into terms that allow the impacts of these flows to be assessed. For example, the climate change impacts of GHG emissions, such as CO₂, methane and nitrous oxide can be converted to CO₂-equivalent units (e.g. tCO₂-eq) using global warming potential (GWP) or global temperature change potential (GTP).¹⁰ Other frequently considered impact categories include ozone depletion, acidification, eutrophication, fossil fuel depletion and human health.

For the results of the impact assessment to be useful, they should also be summarized in a way that is suitable, considering the goals and scope of the LCA and any limitations highlighted. While not a requirement of the ISO Standard, it is a best practice to explore the results of uncertainty and variability in data and models on the results.¹¹ Ignorance of the potential ranges of results (and their distribution) can lead to poor decisions, particularly in product-comparison studies. The inadequate treatment of uncertainty in

LCA of biofuels and LCFS-like policies has been the focus of much criticism.¹²

LCA can be undertaken for a wide variety of reasons, such as to identify “hotspots” and opportunities for improvement through R&D or design changes, inform purchasing decisions through product footprinting, identify strategic opportunities to improve sustainability in product portfolios (e.g. reducing the wash cycle temperature for detergents), guide public R&D investment, and inform policy making.¹³ Traditional environmental LCA, however, isn’t a substitute for cost-benefit analysis, risk assessment or environmental impact assessment and—like all of these tools—provides information that must be carefully weighed by decision makers.

Developing consistent LCAs for CO₂-based products

LCA of CO₂-based products presents a number of methodological challenges, many of which were highlighted in the first version of this roadmap and other reviews.¹⁴ The following section recaps these challenges, along with suggested solutions to address them.

The first challenge is treatment of the CO₂ feedstock. Whether CO₂ should be treated as a “waste” or a “commodity” is a question that has been debated in the context of CCS.¹⁵ However, where captured CO₂ is the feedstock for a CO₂-based product, it should be treated like any other feedstock.¹⁶ Thus, the source of the CO₂ and the environmental impact of capturing the CO₂ matters. For example, von der Assen et al.¹⁷ estimate that, relative to a case in which CO₂ was emitted, capturing CO₂ from an existing industrial facility in the EU would reduce emissions by between 0.42 tCO₂-eq and 0.99 tCO₂-eq per ton of CO₂ supplied, depending on the type and location of the facility.¹⁸ The environmental impact of CO₂ supply should be addressed by including the CO₂ capture process within the boundaries of the LCA, and where the source of CO₂ is not known, a range of sources should be considered.

The multiple-product nature of CO₂U systems can also pose a challenge. This may occur where CO₂ capture cannot be separated from production of a “primary product” (e.g. steel) due to the goals and scope of the

study. In such a case, the system will have multiple products (e.g. steel and methanol). Even where CO₂ capture can be separated analytically, the CO₂ utilization process may also result in multiple products, for example, where CO₂ is converted to syncrude using a Fischer-Tropsch process. In such cases, generating accurate LCA results for the product of interest (e.g. gasoline) requires the lifecycle inventory to either be allocated across all the products from the system or the boundaries of the system expanded to include all the products.

For multiple-product systems, the ISO Standard recommends system expansion over allocation,¹⁹ as different approaches to allocation can result in very different results for the same system. When faced with a comparable problem in the context for a study on CO₂ storage through enhanced oil recovery (EOR), Cooney et al. expanded the boundaries of their system to include the electricity generation lifecycle and credited the by-product CO₂ (from electricity generation) with the avoided burden of producing electricity using a range of alternative approaches.²⁰ The clear benefit of the avoided burden approach is that the functional unit is simplified to a single product, which usually makes the results more easily comparable and is generally a sensible approach for CO2U.²¹

Another significant challenge for LCA of CO₂-based products is the assessment of consequential effects. CO₂-based products may displace other products in the market and, if so, that displacement will have an environmental impact that should be attributed to the CO₂-based product. However, determining whether and which other products are displaced will depend on elasticities of demand and other factors for which data may be limited. Determining the environmental impact of the displaced product may not be easy or straightforward either. Additionally, at least in theory, this would require results from a consistent LCA for the displaced product.

For globally traded products, such as the CO₂-based products considered in this roadmap, estimating the change in consumption (and hence emissions) requires an economic model. Given the uncertainties inherent in such models, estimation also demands careful treatment of uncertainty. Consequential effects can be significant, as illustrated in the case of biofuels²² and enhanced oil recovery (EOR).²³ The need to assess

these consequential effects is an opportunity for the energy systems modeling and LCA communities to work more closely together. Of course, LCA can provide useful insights even without more complex consequential analysis.

A fourth challenge for LCA for CO₂-based products (shared with CCS²⁴ and biofuels)²⁵ is the time dependence of the impact of GHG emissions (or removals). This affects the value associated with temporary removal of CO₂ from the biosphere. The most commonly used measure of climate change impact is the 100-year GWP (GWP100): the cumulative impact of an instantaneous emission of a given GHG on the earth's energy balance over a century, relative to that of CO₂.²⁶ In conventional LCA, a constant GWP is used to convert inventory to climate impacts, regardless of when the emission occurs, and ignores the benefit of delaying emissions through temporary storage, implying a temporal mismatch between the period over which the LCA is being performed and that of the impacts assessed. While a 100-year time horizon is commonly used, it is rarely acknowledged that the choice of the time horizon (both for GWP and for the LCA) implies a value judgement about the relative importance of impacts over time.²⁷

In principle, the climate change impact assessment method chosen for LCA should reflect the fact that products in which CO₂ is stored longer have a smaller climate impact (i.e. a larger benefit) than for short-lived products where CO₂ is returned promptly.²⁸ There are multiple different approaches to address this challenge, but consensus has not yet emerged on the most generally appropriate method, and this is an area where guidelines for CO2U could help.²⁹

Fifth, many CO2U processes are at very early stages of technological development. Information about the performance of a CO₂-based product and its production process may be limited; what information is available may be difficult to extrapolate to commercial scales, and future performance may be highly uncertain.³⁰ These factors all make comparisons with more established technologies more difficult. Thus, it is important for LCA to be integrated into the R&D process and for prospective assessments to be carried out as the technology evolves, for the results of LCA to feed back into the R&D process and influence the direction of R&D, for the limitations of such LCA studies to be clearly defined, and, for suitable

sensitivity analysis to be performed that illustrates the full range of possible outcomes.

Finally, while much of this discussion has focused on the climate change impacts of CO₂-based products, other impacts can make or break the commercial success of processes. For example, the conventional route to produce dimethyl carbonate requires phosgene (COCl₂), a highly dangerous substance that was used as a chemical weapon in World War I. In contrast, the CO₂-based route avoids phosgene—moreover, dimethyl carbonate can serve as a substitute for phosgene in synthesis processes.³¹ Similarly, the use of CO₂ in polyurethane production has been shown to reduce a wide range of impacts beyond climate.³² When focusing on climate change impacts, it is important not to lose sight of other environmental impacts.

Examples of LCA for CO₂-based products

In a 2015 critical review of CCUS LCA studies, Cuéllar-Franca and Azapagic identified 16 peer-reviewed LCA studies of CO₂ utilization systems.³³ Three-quarters of these studies dealt with EOR or fuel production from algae (which are outside the scope of this roadmap), leaving only four studies of systems that generated a CO₂-based product.³⁴ Only one of those four studies explicitly considered the CO₂-based product as a product, rather than as a waste from CO₂ capture in electricity generation. This illustrates both the complexity of executing LCAs for CO₂-based products and the novelty of the topic.

A handful of additional peer-reviewed LCA studies have been published (largely subsequent to the writing of the 2015 review) that address:

- **Polyurethane:** The climate change (GWP) and fossil-fuel depletion impacts of using CO₂ directly in polyol production for polyurethane—and indirectly, as a feedstock for other chemicals (e.g. methanol, isocyanates) used to make polyurethane—was investigated by von der Assen et al.³⁵ Their studies conclude that incorporating CO₂ into polyols reduces the GWP of their production relative to conventional, fossil-based processes. It also concludes that using the maximum amount of CO₂ possible in the polyurethane production chain is not the optimal way to reduce GWP.

- **Dimethyl ether (DME):** The environmental performance of direct DME synthesis from syngas in a refinery complex (where the syngas is produced from dry reforming of methane³⁶ and CO₂ captured from hydrogen production) was investigated by Schakel et al.³⁷ Production of CO₂-based DME has a smaller GWP than DME produced from a conventional route (i.e. dehydration of methanol) and the CO₂ emitted (rather than captured). However, it has substantially poorer environmental performance in some other areas, particularly with regard to water impacts, resulting from increased electricity demand and rare-earth metal demands for catalyst production. They also found that the GWP of DME produced via the conventional route and the CO₂ captured and stored (rather than being used) is much lower than the CO₂-based DME.

- **Carbon monoxide, formic acid, methanol and methane:** The climate change (GWP) and fossil-fuel depletion impacts of these chemicals has been evaluated in three, partially overlapping studies. Two of the studies evaluate the emissions reduction potential and economics of direct thermocatalytic methanol production and electrochemical formic acid production; however, only one, performed for the French Environment and Energy Management (ADEME), considers the full product lifecycle, including CO₂ supply.³⁸ This study concluded that substitution of both CO₂-based products for their fossil-based equivalent would result in emissions reductions with the use of low-carbon French grid electricity—1.4 tCO₂ avoided per ton of fossil methanol displaced, and 2.75 tCO₂ avoided per ton of formic acid displaced. The third study evaluated thermocatalytic production of all four products, with the goal of identifying which product's substitution could result in the largest benefit and where a limited supply of low-carbon hydrogen would have the largest impact. They find that only CO₂-based formic acid has a lower GWP than its conventional fossil-based equivalent in the base case, but that this conclusion is relatively robust to changes in hydrogen supply. At the other end of the spectrum, they find that CO₂-based methane produced with CO₂ captured from the air has GWP lower than fossil methane—but only if wind electricity is used to produce hydrogen via electrolysis across all CO₂-supply and process scenarios (i.e. electricity

generated from solar PV doesn't have a sufficiently low GWP).

- **Carbonate minerals:** The energy efficiency and CO₂ storage potential production of carbonate minerals using a range of different aqueous carbonation processes, using different alkalinity sources (natural silicates, cement kiln dust, fly ash and steel slag) was compared by Kirchofer et al.³⁹ They considered these processes as a means of CO₂ storage (rather than a utilization option) and, thus did not consider the environmental burdens of CO₂ capture. Nonetheless, they found that, on balance, these processes resulted in an absolute emissions reduction (since the CO₂ is permanently bound in mineral form) and that there is significant room to improve the environmental performance of mineralization processes through optimization.

While these recent studies add to the knowledge base for CO₂-products, they also support some of the criticisms of Cuéllar-Franca and Azapagic, such as the need for consistency in functional units for different CO₂-based products and (as already mentioned) inclusion of the CO₂-supply process in study scopes.⁴⁰ In addition, given early stage of technology development for most CO₂-based production processes (and many CO₂-capture processes), LCA studies should better characterize the uncertainties in their results and potential areas for improvement.

Findings and recommendations

Findings

LCA is an important tool to quantify the climate change impacts of CO₂-based products. It can also be used to focus R&D in areas that could bring about the greatest benefits. ISO standards and guidance exist for LCA practitioners that, if followed, can improve the quality of an LCA and improve the chances that the results will be accurate and robust. However, there is a need to refine this guidance for CO2U applications.

Based on our review of LCA for CO₂-based products, we suggest that:

- CO₂ supply (i.e. capture and transport) should be within the scope of an LCA that aims to estimate the climate change impacts of a CO₂-based product;
- Existing guidance (e.g. provided in ISO standards, government agency guidance, and peer-reviewed

literature) around LCA boundary expansion and, if necessary, allocation should be followed (including transparent, justifiable choices for avoided burdens);

- Where the LCA seeks to inform decisions that could have impacts to the broader market (e.g. government policy), the impacts of displacement of other products should be considered in an LCA; and,
- The CO2U and broader LCA communities agree upon an approach to climate-impact assessment that places an appropriate value on temporary storage of CO₂ in products.

In addition, while the current motivation for CO₂-based products means that climate impacts are typically presented first and foremost in LCA studies of these systems, other environmental impacts are important and can be pivotal in decision-making. Provision of product footprints affects the purchasing decisions of informed consumers.

Peer-reviewed LCAs have been performed for very few CO₂-based products. From the few that have been performed, several general conclusions can be drawn for CO₂-based products:

- Maximizing CO₂ use in the production chain does not necessarily maximize avoided emissions;
- The benefits of CO₂ use can appear where one doesn't expect them – e.g. by reducing cement consumption;
- Benefits of CO₂ use can be maximized by making CO₂-based products that substitute for fossil equivalents with complex and energy intensive production systems;
- The carbon intensity of electricity (and hydrogen) supply is very important.

Additional studies are required that guide R&D towards products and processes that are likely to have the largest environmental benefit.

Recommendations

To support the goal of advancing the near-term commercialization and long-term potential of CO₂-based products:

- Research funding bodies should provide support for additional studies of CO₂-based products and production pathways with the aim of directing R&D.

- Consensus guidelines should be developed that elaborate on the application of the existing ISO standards and related guidance to LCA for CO₂-based products and production systems.
- LCA studies that aim to make comparative statements about the emissions reduction benefits of CO₂-based products relative to others should, ideally, present probabilistic uncertainty analysis that captures the impact of different CO₂-supply options (where these are not fixed by scope), electricity supply mixes, and hydrogen (or mineral) supply options. Where fully probabilistic treatments of uncertainty are not practical, alternative sensitivity analysis approaches should be used (e.g. bounding analysis).
- The LCA and energy-modeling communities should work together to better represent CO₂ utilization options in energy systems models and better understand the boundary conditions for CO₂ utilization processes in the future energy system—particularly as a means of improving consequential LCA for CO₂-based products.
- The CO₂ utilization community and the LCA practitioners working with them should be cognizant of the lessons learnt from LCA of biofuels and CCS—these systems share many of the same features.

¹ André Sternberg, Christian M. Jens, and André Bardow, “Life Cycle Assessment of CO₂-Based C1-Chemicals,” *Green Chemistry* 19, no. 9 (May 8, 2017): 2244–59, doi:10.1039/C6GC02852G.

² ISO, “Environmental Management — Life Cycle Assessment — Principles and Framework” (International Standards Organization, July 1, 2006); ISO, “Environmental Management — Life Cycle Assessment — Requirements and Guidelines” (International Standards Organization, July 1, 2006).

³ JRC, “ILCD Handbook: General Guide for Life Cycle Assessment - Detailed Guidance” (Luxembourg: European Commission - Joint Research Center, March 2010), <http://eplca.jrc.ec.europa.eu/uploads/ILCD-Handbook-General-guide-for-LCA-DETAILED-GUIDANCE-12March2010- ISBN-fin-v1.0-EN.pdf>.

⁴ U.S. EPA, “Life Cycle Assessment: Principles and Practice” (Cincinnati, OH: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, May 2006).

⁵ “DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 November 2008 on Waste and Repealing Certain Directives,” 2008/98/EC § (2008), <http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32008L0098&from=EN>.

⁶ “Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 Amending Directive 98/70/EC as Regards the Specification of Petrol, Diesel and Gas-Oil and Introducing a Mechanism to Monitor and Reduce Greenhouse Gas Emissions and Amending Council Directive 1999/32/EC as Regards the Specification of Fuel Used by Inland Waterway Vessels and Repealing Directive 93/12/EEC,” 2009/30/EC § (2009), <http://data.europa.eu/eli/dir/2009/30/oj>.

⁷ “Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the Promotion of the Use of Energy from Renewable Sources and Amending and Subsequently Repealing Directives 2001/77/EC and 2003/30/EC,” 2009/28/EC § (2009), Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC..

⁸ “Low Carbon Fuel Standard,” Title 17 California Code of Regulations § 95480-95497 (2015), [\(https://govt.westlaw.com/calregs/Document/IC4D9979005294A50AB577FEB54E745B5?view=Type=FullText&originationContext=documenttoc&transitionType=CategoryPageItem&contextData=\(sc.Default\)\)](https://govt.westlaw.com/calregs/Document/IC4D9979005294A50AB577FEB54E745B5?view=Type=FullText&originationContext=documenttoc&transitionType=CategoryPageItem&contextData=(sc.Default)).

⁹ Niklas von der Assen et al., “Life Cycle Assessment of CO₂ Capture and Utilization: A Tutorial Review,” *Chem. Soc. Rev.* 43, no. 23 (January 20, 2014): 7982–94, doi:10.1039/C3CS60373C.

¹⁰ Gunnar Myhre et al., “Anthropogenic and Natural Radiative Forcing,” in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. T. F. Stocker et al. (Cambridge, U.K.: Cambridge University Press, 2013), [\(http://www.climatechange2013.org/images/report/WG1AR5_Chapter08_FINAL.pdf\)](http://www.climatechange2013.org/images/report/WG1AR5_Chapter08_FINAL.pdf).

¹¹ JRC, “ILCD Handbook: General Guide for Life Cycle Assessment - Detailed Guidance.”

¹² Kimberley A. Mullins, W. Michael Griffin, and H. Scott Matthews, “Policy Implications of Uncertainty in Modeled Life-Cycle Greenhouse Gas Emissions of

Biofuels," *Environmental Science & Technology* 45, no. 1 (January 1, 2011): 132–38, doi:10.1021/es1024993; Matt Kocoloski et al., "Addressing Uncertainty in Life-Cycle Carbon Intensity in a National Low-Carbon Fuel Standard," *Energy Policy* 56 (May 2013): 41–50, doi:10.1016/j.enpol.2012.08.012; Elliot W. Martin, Mikhail V. Chester, and Sintana E. Vergara, "Attributional and Consequential Life-Cycle Assessment in Biofuels: A Review of Recent Literature in the Context of System Boundaries," *Current Sustainable/Renewable Energy Reports* 2, no. 3 (September 1, 2015): 82–89, doi:10.1007/s40518-015-0034-9.

¹³ Stefanie Hellweg and Llorenç Milà i Canals, "Emerging Approaches, Challenges and Opportunities in Life Cycle Assessment," *Science* 344, no. 6188 (June 6, 2014): 1109–13, doi:10.1126/science.1248361.

¹⁴ Issam Dairanieh et al., "Carbon Dioxide Utilization (CO₂U) – ICEF Roadmap 1.0" (Tokyo, Japan: ICEF Innovation Roadmap Project, 2016), http://www.icef-forum.org/platform/upload/CO2U_Roadmap_ICEF2016.pdf; von der Assen et al., "Life Cycle Assessment of CO₂ Capture and Utilization"; Niklas von der Assen, Johannes Jung, and André Bardow, "Life-Cycle Assessment of Carbon Dioxide Capture and Utilization: Avoiding the Pitfalls," *Energy & Environmental Science* 6, no. 9 (2013): 2721, doi:10.1039/c3ee41151f.

¹⁵ Philip M. Marston, "Bridging the Gap: An Analysis and Comparison of Legal and Regulatory Frameworks for CO₂–EOR and CO₂–CCS" (Canberra, Australia: Global CCS Institute, 2013), <http://decarboni.se/sites/default/files/publications/118951/bridging-gap-analysis-comparisonlegal-regulatory-frameworks-eor-ccs.pdf>.

¹⁶ von der Assen, Jung, and Bardow, "Life-Cycle Assessment of Carbon Dioxide Capture and Utilization"; von der Assen et al., "Life Cycle Assessment of CO₂ Capture and Utilization."

¹⁷ Niklas von der Assen et al., "Selecting CO₂ Sources for CO₂ Utilization by Environmental-Merit-Order Curves," *Environmental Science & Technology* 50, no. 3 (February 2, 2016): 1093–1101, doi:10.1021/acs.est.5b03474.

¹⁸ In this case, a CCS system that generated no GHG emissions during its construction and operation would result in an emissions reduction of 1 tCO₂-eq per tCO₂ captured. However, if the basis for comparison were that, instead of being emitted, the captured CO₂ was

be stored in a saline aquifer the CO₂ there would be no climate benefit to using captured CO₂ as a feedstock.

¹⁹ ISO, "Environmental Management — Life Cycle Assessment — Requirements and Guidelines."

²⁰ Gregory Cooney et al., "Evaluating the Climate Benefits of CO₂-Enhanced Oil Recovery Using Life Cycle Analysis," *Environmental Science & Technology* 49, no. 12 (June 16, 2015): 7491–7500, doi:10.1021/acs.est.5b00700.

²¹ von der Assen et al., "Life Cycle Assessment of CO₂ Capture and Utilization."

²² Richard J. Plevin, Mark A. Delucchi, and Felix Creutzig, "Using Attributional Life Cycle Assessment to Estimate Climate-Change Mitigation Benefits Misleads Policy Makers," *Journal of Industrial Ecology* 18, no. 1 (February 1, 2014): 73–83, doi:10.1111/jiec.12074.

²³ IEA, "Storing CO₂ through Enhanced Oil Recovery" (Paris, France: International Energy Agency, 2015), <https://www.iea.org/publications/insights/insightpublications/storing-co2-through-enhanced-oil-recovery.html>.

²⁴ H. Herzog, K Calderia, and J. Reilly, "An Issue of Permanence: Assessing the Effectiveness of Temporary Carbon Storage," *Climatic Change* 59 (2003): 293–310; Minh Ha-Duong and David W. Keith, "Carbon Storage: The Economic Efficiency of Storing CO₂ in Leaky Reservoirs," *Clean Technologies and Environmental Policy* 5, no. 3–4 (2003): 181–89; Fei Teng and Daniel Tonneur, "Efficiency of Carbon Storage with Leakage: Physical and Economical Approaches," *Energy* 32, no. 4 (2007): 540–48.

²⁵ Miguel Brandão et al., "Key Issues and Options in Accounting for Carbon Sequestration and Temporary Storage in Life Cycle Assessment and Carbon Footprinting," *The International Journal of Life Cycle Assessment* 18, no. 1 (June 2, 2012): 230–40, doi:10.1007/s11367-012-0451-6.

²⁶ Myhre et al., "Anthropogenic and Natural Radiative Forcing."

²⁷ *Ibid.*

²⁸ von der Assen, Jung, and Bardow, "Life-Cycle Assessment of Carbon Dioxide Capture and Utilization."

²⁹ Brandão et al., "Key Issues and Options in Accounting for Carbon Sequestration and Temporary Storage in Life Cycle Assessment and Carbon Footprinting."

³⁰ Alexandra C. Hetherington et al., "Use of LCA as a Development Tool within Early Research: Challenges and Issues across Different Sectors," *The International Journal of Life Cycle Assessment* 19, no. 1 (January 1, 2014): 130–43, doi:10.1007/s11367-013-0627-8; Ben A. Wender et al., "Anticipatory Life-Cycle Assessment for Responsible Research and Innovation," *Journal of Responsible Innovation* 1, no. 2 (May 4, 2014): 200–207, doi:10.1080/23299460.2014.920121.

³¹ Evan S. Beach, Zheng Cui, and Paul T. Anastas, "Green Chemistry: A Design Framework for Sustainability," *Energy & Environmental Science* 2, no. 10 (2009): 1038–49, doi:10.1039/B904997P.

³² Niklas von der Assen and André Bardow, "Life Cycle Assessment of Polyols for Polyurethane Production Using CO₂ as Feedstock: Insights from an Industrial Case Study," *Green Chemistry* 16, no. 6 (2014): 3272, doi:10.1039/c4gc00513a.

³³ Rosa M. Cuéllar-Franca and Adisa Azapagic, "Carbon Capture, Storage and Utilisation Technologies: A Critical Analysis and Comparison of Their Life Cycle Environmental Impacts," *Journal of CO₂ Utilization* 9 (March 2015): 82–102, doi:10.1016/j.jcou.2014.12.001.

³⁴ Michele Aresta and Michele Galatola, "Life Cycle Analysis Applied to the Assessment of the Environmental Impact of Alternative Synthetic Processes. The Dimethylcarbonate Case: Part 1," *Journal of Cleaner Production* 7, no. 3 (March 1999): 181–93, doi:10.1016/S0959-6526(98)00074-2; Hsien H. Khoo and Reginald B.H. Tan, "Life Cycle Evaluation of CO₂ Recovery and Mineral Sequestration Alternatives," *Environmental Progress* 25, no. 3 (October 1, 2006): 208–17, doi:10.1002/ep.10139; Hsien H. Khoo et al., "Carbon Capture and Mineralization in Singapore: Preliminary Environmental Impacts and Costs via LCA," *Industrial & Engineering Chemistry Research* 50, no. 19 (October 5, 2011): 11350–57, doi:10.1021/ie200592h; Experience Nduagu, Joule Bergerson, and Ron Zevenhoven, "Life Cycle Assessment of CO₂ Sequestration in Magnesium Silicate Rock – A Comparative Study," *Energy Conversion and Management* 55 (March 2012): 116–26, doi:10.1016/j.enconman.2011.10.026.

³⁵ von der Assen and Bardow, "Life Cycle Assessment of Polyols for Polyurethane Production Using CO₂ as Feedstock"; Niklas von der Assen et al., "Environmental Potential of Carbon Dioxide Utilization in the Polyurethane Supply Chain," *Faraday Discussions* 183, no. 0 (2015): 291–307, doi:10.1039/C5FD00067J.

³⁶ In dry reforming of methane, CO₂ and methane are combined at high temperature over nickel based catalysts producing a roughly 1:1 mixture of hydrogen and syngas. Refer to Section 2.2 for additional detail on uses of dry reforming in CO₂-based processes.

³⁷ Wouter Schakel et al., "Assessing the Techno-Environmental Performance of CO₂ Utilization via Dry Reforming of Methane for the Production of Dimethyl Ether," *Journal of CO₂ Utilization* 16 (December 2016): 138–49, doi:10.1016/j.jcou.2016.06.005.

³⁸ Guillaume Kerlero de Rosbo et al., "Valorisation Chimique Du CO₂: Etat Des Lieux – Quantification Des Bénéfices Énergétiques et Environnementaux et Évaluation Économique de Trois Voies Chimiques" (Angers, France: Agence de l'Environnement et de la Maîtrise de l'Energie, 2014), <http://www.ademe.fr/valorisation-chimique-co2-etat-lieux-quantification-benefices-energetiques-environnementaux-evaluationeconomique-trois-voies-chimiques>; Mar Pérez-Fortes and Evangelos Tzimas, "Techno-Economic and Environmental Evaluation of CO₂ Utilisation for Fuel Production: Synthesis of Methanol and Formic Acid" (European Commission Joint Research Centre, 2016), <https://dx.doi.org/10.2790/981669>.

³⁹ Abby Kirchofer et al., "Impact of Alkalinity Sources on the Life-Cycle Energy Efficiency of Mineral Carbonation Technologies," *Energy & Environmental Science* 5, no. 9 (2012): 8631–41, doi:10.1039/C2EE22180B.

⁴⁰ Cuéllar-Franca and Azapagic, "Carbon Capture, Storage and Utilisation Technologies."

Chapter 6:

General R&D Needs for CO₂ Utilization

In addition to the detailed research and development (R&D) needs cited in each chapter, we have identified a set of cross-cutting R&D needs that apply broadly to CO₂ utilization.

Analysis

The most immediate R&D need in this area is for better analytical tools to understand the benefits of CO₂ utilization. This is critical for governments and other actors who want to encourage this as a means of emissions management. Today, there are few end-to-end analyses of the emissions benefit of utilization schemes. Moreover, there is no universally accepted approach to evaluating the benefit of turning carbon dioxide into products that are long-lived, but not permanently removed from the atmosphere.

The experience in California with the Low Carbon Fuel Standard (LCFS) demonstrates that once clear metrics are put in place, it is feasible to drive technology to better and better outcomes. The average carbon intensity (CI) of alternative fuels being utilized in California has fallen 21% since the implementation of the LCFS program, in no small part due to technological innovation in fuel production.¹ For example, the CI of the best performing corn-based ethanol pathways certified under the LCFS has fallen over time and is now approaching 40% below that of gasoline. A vitally important aspect of the success of the LCFS program is the standardized approach to life cycle assessment, based on the GREET model, allowing the CI of a wide range of alternative fuels to be consistently estimated. While aspects of the LCFS remain controversial and ways to improve it have been suggested,² the LCFS experience demonstrates that thoughtful and uniformly applied life cycle assessment is important to both policy and technology development.

Unfortunately, a consistent approach to LCA doesn't yet exist for the CO₂ utilization schemes described here. This is attributable to the facts that CO₂ utilization concepts are still relatively nascent

(at least compared to biofuels), there is a relative dearth of policy mechanisms that might drive their commercial deployment, and there is still debate over methodological issues (e.g. consequential effects, valuation of temporary GHG removals, end-of-life treatment). Issues that should be addressed as part of developing a consistent approach include:

- Agreement over the appropriate goals and scope for LCA for CO₂U.
- Consistent sets of assumptions for the environmental burden of CO₂ supply that reflect the best estimates for current (and future) CO₂ capture technologies.
- Consistent sets of assumptions for the environmental burdens associated with energy inputs—electricity, in particular—and hydrogen.
- Agreement on assessing the impacts of temporary CO₂ storage in CO₂-based products.

With such guidelines in use, more general comparisons can be made between different CO₂-based product options than can be made with the few focused assessments that are available today.

In addition to guidelines that enable more focused LCA, studies are needed of the path to deployment for the processes discussed here. The use of CO₂ based products at gigaton scale will link energy and materials production in a way that is seldom considered in existing energy systems models and will ripple across the economy. These waves will be magnified where the uses of CO₂-based materials enable the provision of services in a different or more efficient way (e.g. durable carbon materials). This is the domain of techno-economic and systems analysis. Such analysis will allow more specific roadmaps to be developed based on sensible long-term goals, and key questions to be answered. For example, are there obvious supply chain or geographic resource choke-points that would limit deployment? Which policy mechanisms make the most sense to drive deployment? Where might R&D have the biggest payoffs?

Catalysis

Many of the most interesting utilization schemes involve catalysis. Most CO₂-to-product conversions have high activation energies, small yields and additional separation steps. The design of better catalysts in general would greatly reduce the overall practical energy requirements and capital costs,

making CO₂ conversions much more efficient than today. This remains a major need for CO₂U.

There are four catalytic pathways for CO₂U: thermal, electrical, photolytic and biological (refer to Section 2.2).

- Thermal approaches are the most mature and, for some processes, are commercial today at small scales (e.g. for CO₂-to-methanol). Many are high-temperature processes (above 500 °C), so lower-temperature catalysts require more focus. High selectivity is also a specific challenge (e.g. with Fischer-Tropsch conversion).
- Electrical pathways have emerged as an important new research focus, in part due to the increased availability of low-cost renewable power. In addition to the need for lower overvoltage and greater selectivity, many electrical pathways today are slow, so catalysts with improved kinetics are a special need. Finally, new materials for both anodes and cathodes require development.
- Most photolytic pathways require substantial research to improve cost, performance, yields and rates. Many candidate catalysts involve exotic and expensive materials. Much of the current research is at a very early stage, and it is unclear how to dramatically improve performance without more basic research (or how to functionalize those catalysts that show promise).
- Biological pathways often have very good kinetics but low yields and restrictions in temperature, pressure and pH. Again, much of this R&D is at a very early stage, and would benefit from use-inspired basic R&D.

Today, the energy usage of those catalytic schemes is dominated by two energy penalties: one associated with high temperatures and the other with electrical overvoltage. Reducing overvoltage and temperature for catalysts is part of many research programs, and should be strongly encouraged as a near-term focus, given the maturity of thermal approaches and the near-term promise of electrical ones. In many cases, the simultaneous reduction of CO₂ and disassociation of water may be achieved beneficially in a single process. Methods to make efficient use of electrical energy in processes like that are required.

Two scientific approaches could greatly enhance and accelerate design of catalysts. The first is computational material design, in which large

supercomputers perform very large numbers of simultaneous calculations to find promising new molecular configurations. Tens of thousands of materials can be analyzed each week, providing direction and design specifications for chemists to build and test the new materials. The second approach is high-throughput experimentation, which allows investigators to simultaneously test hundreds of candidate materials with the assistance of robots, big data and parallel processing. Both approaches enhance the effectiveness of searches for new CO₂-conversion catalysts, and should be more formally incorporated into R&D programs.

Reactor design advances

The development of thermal, electrical, biological and photolytic catalysts represents the first stage of development, and commonly focus on low levels of technical readiness (i.e. near the benchtop). Full-scale application requires considerable attention to the integrated systems (reactors) that will utilize those catalysts. Most products today that take advantage of conventional conversion media, such as syngas-to-methanol reformers, batch reactors, or reverse fuel cells, are based on approaches developed 20-80 years ago. Often, these conventional approaches have substantial shortcomings associated with capital cost, industrial scale-up, and mass-manufacturing.

Technological advances from 3D printing, microfluidics, genetic engineering and computational design make possible reactors and processes which are radically different from conventional approaches. Many research programs lack access to these techniques and technologies. A novel reactor-design program aimed at moving from low to high levels of technical readiness could deliver the dramatic reductions of cost and increases in performance and yields needed to gain market parity for CO₂-derived products. A priority should be given to functionalizing existing materials through new means, and to continuous production approaches (as opposed to batch processes).

Process intensification

Most reactions where CO₂ is a reactant rather than a product are either thermodynamically unfavorable or kinetically slow. Thus, making practical processes based around these reactions requires large reactors, energetically expensive separations and

large materials inventories in recycle loops. Process intensification approaches that combine otherwise separate chemical engineering unit operations (e.g. reactions with separations) can address these issues. For example, production of carbon monoxide from CO₂ by the reverse water gas shift reaction could be substantially improved by the removal of water from the reactor, as could almost all low-temperature electrochemical conversion routes. Another example is the combination of CO₂ separation with reactions to produce intermediates in CO2U processes or CO₂-based products. Research and development should focus on identifying opportunities for process intensification in CO2U.

New methods for elemental carbon production

Although durable carbon materials are an attractive future form of carbon utilization, today there are limited approaches for converting CO₂ directly into carbon products. Significant levels of basic research in this area could be expected to result in new pathways and increased usability of the carbon produced by existing pathways. The benefits of this research will be as important to efficiency as to carbon utilization, and it should be prioritized accordingly. A future economy where carbon fiber is cheap enough to be a common component of automobiles is indeed attractive.

Because of the early stage of this research, it will be necessary to plan for scale-up and production R&D efforts as the bench results become available. Early work in examining the synergies with molten carbonate fuel cells is an early avenue to pursue here.

Materials substitution

While some CO₂-based products compete directly with essentially identical products (for example, formic acid), others will offer improved performance. One example is the use of new building materials such as carbon-fiber-reinforced concrete, which can substitute for conventional rebar (steel-reinforced concrete) and allow advances in design and cost reductions, while delivering emissions-reduction benefits across the life cycle. Similarly, the use of carbon fiber instead of steel or aluminum in automobile construction leads to lighter vehicles and obvious energy savings. Identifying use cases where CO₂-based products can substitute for materials that are significantly different,

while providing equal or improved performance, is an important area for further research. The consideration of how to make those materials with low-emissions processing should be an important part of the evaluation of their usefulness. The use of carbon-based materials created by nature, although not considered in this report, shares that same need for simultaneous analysis of efficiency, lifetime and emissions footprint.

Low-carbon energy supply and delivery

Many CO₂ schemes are predicated on a large supply of low-cost, low-carbon renewable electricity. While the cost of renewable electricity is falling rapidly and the installed capacity is growing almost everywhere in the world, the character of the energy delivered is variable by its nature and not suitable for conventional 24-7 industrial operations. For example, high temperature systems (e.g. electrolyzers) are best operated at relatively steady state, and are much less efficient and reliable when operated variably. Schemes to provide low-carbon electricity with characteristics suitable for industrial-scale operations must be developed. This could be via facility-level integrated systems of renewable generation with sufficient storage capacity to maintain industrial production, or continued development of such systems at the grid scale. Adaptation of CO2U processes to better handle variable electricity inputs is also critical.

The energy delivery challenge could also be mitigated by the placement of CO2U facilities in optimal locations where a steady low-carbon energy supply is available. It is possible that the regional availability of low-carbon energy will drive the placement of carbon-utilization industries (as it has in other sectors, such as aluminum smelting).

Collocating and integrating CO2U with CO₂ capture

Most studies of CO₂ utilization assume that CO₂ is readily available, but, unless it is captured from the air, it will always have to be transported and occasionally stored. For example, compression and transport of CO₂ over long distances is particularly costly, especially where it is decompressed for use. Thus, it may be advantageous to co-locate carbon capture and utilization facilities, even making utilization part of the carbon-capture process, avoiding CO₂ transport

altogether. For instance, many hydrogenation schemes are exothermic, making process heat available for other activities. Integration with a carbon-capture system using heat (e.g. to regenerate solvents) could make excellent use of that resource.

Discussions about the synergies between CO₂U processes and CO₂ capture have been focused on integration with power plants, but it is clear that CO₂ utilization will be a significant part of industrial sectors beyond electricity generation. These integration options need to be explored. These industrial synergies may have major impacts on the economics of specific CO₂ utilization approaches.

Reducing the CO₂ footprint for raw materials

A similar problem arises for the use of CO₂ to make aggregate and cements requiring additional magnesium and calcium. These additional materials are heavy and not available everywhere. While those cations are widely available in oceans and volcanic rocks, it is not easy to extract them for use. In the case of oceans, removing them releases CO₂ to the atmosphere—improved methods are needed to avoid this problem. In the case of rocks, methods are needed to remove the useful cations for use elsewhere, or to bring CO₂ and the rocks together by some means. The movement of goods or CO₂ across large distances is a major detractor from the climate benefit of CO₂U. Research on approaches that minimize the carbon footprint from the supply of raw materials is needed.

Tools for lifecycle validation

Today assessment of the life cycle impact of products is typically based on bottom-up modeling of materials and energy flows, often using relatively sparse data. There are few tools to analytically determine the ultimate carbon content of products, and the origin of that carbon. This is particularly important in products like concrete, where there are many opportunities for CO₂ to escape from the process. This is complicated by the fact that the raw materials for concrete and aggregates (such as limestone) naturally contain substantial amounts of carbon, some of which is

carried over into the product. The amount added can therefore be a small difference.

Measurements of how much CO₂ was deliberately added to a product could take the form of isotopic measurements, or validated difference measurements for production systems. Concrete and aggregates are a particularly difficult case because the materials are hard and cannot easily be dissolved for analysis. Small differences in carbon content can have a large impact on carbon utilization in such a large market. These validation tools may be thought of as partially “closing the books” on the life cycle analysis tools that was discussed at the beginning of the chapter.

Regulation and standards

Finally, virtually all markets mentioned here are touched by regulation and voluntary standards, the impacts of which must be clearly understood if CO₂U is to be successful. In general, individual developers take a very large risk in trying to get new classes of products accepted in the necessarily complex regulated and standardized markets for construction and high-strength materials. Collaborative efforts between engineers, scientists and policy experts to synthesize information on CO₂-based products and their potential contributions to the portfolio of climate solutions is needed.³ Research in this space can also contribute to the development of new approaches to performance-based regulations and standards—reducing barriers to entry in the market for new and innovative products or products made in new ways, such as CO₂-based products.

¹ Sonia Yeh et al., “A Review of Low Carbon Fuel Policies: Principles, Program Status and Future Directions,” *Energy Policy* 97 (October 2016): 220–34, doi:10.1016/j.enpol.2016.07.029.

² Matt Kocoloski et al., “Addressing Uncertainty in Life-Cycle Carbon Intensity in a National Low-Carbon Fuel Standard,” *Energy Policy* 56 (May 2013): 41–50, doi:10.1016/j.enpol.2012.08.012; Yeh et al., “A Review of Low Carbon Fuel Policies.”

³ See, for example the work of the EnCO2re project: <http://enco2re.climate-kic.org/>

Chapter 7:

Policy Options

Well-designed policies can help start and build markets for CO₂U products. Poorly-designed policies can stifle such markets. The details of government policies—on R&D, taxes, regulation, procurement and more—will play an important role in the growth of CO₂U product markets in the decades ahead.

The case for policies to support CO₂U products is strong. First, CO₂ emissions are a classic externality. Market forces alone will not control CO₂ emissions.¹ Second, R&D is essential for many CO₂U products. Yet companies do not invest in the socially optimal level of R&D, especially early-stage R&D, in part because they are unlikely to see results within time frames important to most corporate managers.² Government support for R&D is therefore essential. Third, some CO₂U products will compete against well-established incumbents that have benefitted from policy support in years past.

Different policies will be appropriate in different jurisdictions, depending on public attitudes, regulatory traditions and local circumstances. Some countries favor taxes to achieve environmental objectives, for example. Others reject taxes and favor regulatory approaches. Some countries have strong research institutions and deep experience with research and development programs, while others do not.

This chapter describes and discusses nine policies that could play an important role in promoting CO₂U products.

Government support for R&D

National governments spend roughly \$15 billion annually on research and development for clean energy technologies.³ Yet support for R&D on CO₂ utilization is modest. A significant increase in funding in this area could speed deployment of CO₂U technologies and yield important dividends.

This roadmap identifies a number of priority areas for R&D investment for CO₂ utilization. They include:

- Improving the understanding of the process conditions for forming various types of carbon materials;
- Investigating alternative carbonate electrolytes and mixtures;
- Developing pilot-scale electrolysis facilities that can demonstrate higher material throughput for carbon materials;
- Improving design of catalysts for thermochemical pathways;
- Modeling of CO₂ activation on metal surfaces for electrochemistry; and
- Modeling for co-catalysts in photochemical pathways.

In December 2015, heads of state from more than 20 countries announced Mission Innovation, a coalition dedicated to accelerating clean energy innovation. Member governments (including Japan, China, the United Kingdom, Germany and Saudi Arabia) pledged to double R&D on clean energy within five years. The increase in R&D budgets from these countries in the next few years offers an important opportunity to scale up government R&D funding for CO₂ utilization, including in the areas noted above. A focus on CO₂



utilization could form an important part of the R&D portfolio of all Mission Innovation governments.

In November 2016, the Mission Innovation countries committed to seven Grand Challenges, including one for CCUS with a focus on CO2U.⁴ In September 2017, the United States and Saudi Arabia co-chaired a Mission Innovation CO2U workshop in Houston attended by experts from many nations. The workshop provided material to assist Mission Innovation in expanding R&D on CO2U.

The United States helped launch Mission Innovation and remains a member. Although the U.S. is unlikely to fulfill its overall doubling pledge under the Trump administration, the U.S. Department of Energy awarded \$5.9 million in grants for CO2U projects in February 2017 and an additional \$4.8 million for CO2U projects in August 2017.⁵ CO₂ utilization has won bipartisan support in the U.S. Congress and could be an area in which U.S. government R&D spending will increase in the years ahead.

Carbon price

A price on carbon dioxide emissions, whether through an emissions trading program or tax mechanism, provides an important incentive to cut emissions. Carbon pricing programs are now in place in the European Union, California, nine northeastern U.S. states, most of Canada and seven Chinese provinces. The Chinese government plans to launch a nationwide emissions trading program for carbon dioxide in 2017.

A carbon price can create incentives for CO₂ utilization in two ways. First, capturing CO₂ and using it in an economically valuable product could be the cheapest compliance strategy for some emitters. In the short-term this may be unlikely in most cases due to the high cost of CO₂ capture and conversion. However as capture and conversion costs decline, there will be more instances in which this is a company's best compliance strategy. Second, a carbon price may help incentivize private-sector investments in research and development on CO₂ utilization, if market participants expect the price to endure for the medium or long term.

Carbon pricing regimes do not automatically provide incentives for CO₂ utilization. That depends on their structure and details. The European Union's Emissions Trading Scheme, for example, credits a CO₂ source for any CO₂ transferred from its facility "for the

purpose of long-term geological storage." No credit is available for CO₂ transferred for use in CO₂ products.⁶ If policymakers wish to provide credits for CO₂ used in products in carbon-pricing regimes, they will generally need to specify that as part of the program design.

Tax incentives

Tax incentives can play an important role in helping spur development of clean-energy products. In Norway, for example, generous tax incentives helped electric vehicles capture more than 40% of the new car sales market in 2016. Such incentives could play a similar role in building the market for CO₂ products. Tax incentives could be available to companies that invest in R&D for CO₂ utilization, for example. They could also be available to buyers or sellers of CO₂ products.

Such a proposal has recently been introduced in the U.S. Congress. Under current U.S. law, tax credits are available for CO₂ used in enhanced oil recovery or sequestered in geologic reservoirs. The FUTURE Act would extend the tax credit to CO₂ sequestered in marketable products, ranging from \$30-50/ton of CO₂ captured and bound.⁷ The bill was introduced in July 2017 with bipartisan support and endorsed by both fossil-fuel companies and environmental groups.

This type of focused, direct incentive can have a significant impact. However, to the extent the objective of the tax credit is to cut CO₂ emissions in the short-term, it will be important to establish eligibility criteria that take into account (i) the life cycle emissions associated with the product, and (ii) the permanence of the removal of CO₂ from the atmosphere due to the product.

Mandates

Government mandates can be effective in helping build markets for clean-energy products. In the United States, many state governments require utilities to purchase a minimum percentage of their power from renewable sources (renewable portfolio standards). In India, a similar requirement is imposed by the Ministry of New and Renewable Energy. These requirements have been important to the early growth of wind and solar power in both countries.⁸

Other experiences suggest caution, however. The United States federal government has mandated the use of cellulosic ethanol in fuel supplies for almost a decade. Nevertheless, the cellulosic ethanol industry

remains in its infancy and waivers to that requirement have been granted on a regular basis. Technology-forcing requirements—in which governments require private actors to meet standards that are not yet technically achievable—have been successful in some instances but not in others.⁹

There may be instances in which government mandates could help build markets for CO₂ products. Large concrete manufacturers could be required to produce a certain amount of their product using CO₂ curing, for example. Makers of carbonate aggregates could be required to produce a certain amount of their product by conversion of CO₂. These processes are well understood and technologically viable today, but they are more expensive than conventional methods and manufacturers have little incentive to adopt them. Government mandates could help overcome that, building markets for the use of CO₂ and driving down costs as use of the technologies scales up.

Pipeline development

To be converted into products, CO₂ must either be used at the point of capture, transported in a vehicle (truck, train or ship) or moved by pipeline. Pipeline networks are likely to be the cheapest way to transport

CO₂ over long distances and could play a critical role in helping CO₂ utilization to flourish.

Today the world's largest CO₂ pipeline network is in the United States, which has 4,500 miles of pipelines linking CO₂ sources to sites for enhanced oil recovery. (See map below.) Roughly 80% of the CO₂ in U.S. pipelines is from natural geologic reservoirs. Europe has roughly 620 miles of CO₂ pipelines, mainly to transport CO₂ to depleted oil and gas fields. (One project in the Netherlands distributes CO₂ from a Shell refinery to over 500 greenhouses.) Early planning is underway to develop a more extensive CO₂ pipeline network in Europe. There are a few CO₂ pipelines in the Middle East, Asia and Australia.¹⁰

For many CO₂U technologies, other reactants besides CO₂ are required, the most common of which is hydrogen. Transporting hydrogen can be accomplished via several methods. It will be important to evaluate the transportation and availability issues surrounding hydrogen for some CO₂U products, and a specific evaluation of options may be required, including pipeline construction; road, rail or ship transportation; and physical co-location with a hydrogen source.

Building pipeline networks can involve coordination among many parties and long lead times. In part as a



result, governments can often play an important role: Governments can:

- Help coordinate planning processes, convening relevant stakeholders;
- Facilitate regulatory approvals; and
- Assist with pipeline financing.

These steps can help launch and build markets for CO₂U products.

Government procurement

In many countries, government procurement makes up more than 10% of GDP.¹² Many governments are large consumers of cement (for construction and infrastructure projects) and liquid fuels (for fleet vehicles and aircraft).

Government purchases can play an important role in starting and building new product markets. First, government purchase contracts can provide developers and manufacturers of new products with an assured market, which can be especially important in securing debt capital. Second, government purchases can help establish standard technical specifications for new products, which can help catalyze efficient supply chains.

Several CO₂U technologies may be especially good targets for government procurements, including CO₂-cured cement and CO₂-based aggregates. These could be included in government procurement guidelines for construction projects.¹³ Governments could also target CO₂-based fuels for procurement. (The U.S. Navy has had a similar program for the purchase of drop-in biofuels.) As technologies mature, this could expand to carbon fiber, chemicals and other products.

Life cycle assessments

As noted previously, evaluating the climate benefits of a CO₂-based product requires a life cycle assessment (LCA). (See discussion in Chapter 5.) Governments could help with LCAs for CO₂ products in at least two ways. First, governments could help standardize methodologies for life cycle assessments, by convening relevant stakeholders and issuing reports or guidelines based on the inputs received. (This should be pursued in coordination with private-sector efforts to improve and standardize CO₂U LCA, such as the efforts by The

Global CO₂ Initiative and X Prize.) Second, governments could help fund research on LCAs for individual CO₂ products or product categories. These LCAs may depend on data that is expensive or difficult for private parties to collect, giving governments a potentially important role.

In addition, policy design with respect to CO₂ utilization must pay close attention to the need for LCAs. To the extent that the goal of government policies promoting CO₂ utilization is short-term reduction of CO₂ emissions, LCAs are essential. The FUTURE Act mentioned above provides that the U.S. Department of Energy and U.S. Environmental Protection Agency will develop guidelines for LCAs in connection with the award of tax credits for CO₂ utilization.¹⁵

Certification and testing

Certification plays an important role in many product markets, from electronics and pharmaceuticals to food and sustainable forest products. Certifiers typically validate product quality and/or compliance with certain criteria. Widely used certification organizations include UL, ASME and ASHRAE.

In addition to assuring quality or compliance, certification can act as a market barrier. New products must often go through multi-year assessment and testing processes to ensure that standards are met. These processes perform important social functions—including safety assurance—but can slow the adoption of products made in new ways, such as with CO₂.

Governments typically do not run certification processes or dictate results. However, governments can fund the testing of products by organizations such as UL, ASTM, ASME and ASHRAE in order to help facilitate or speed the certification process. This could be especially important for CO₂-based concrete or carbonate aggregates, which will need to demonstrate compliance with industry quality standards before widespread adoption. In particular, government support could include international meetings and discussions to help facilitate commercial development and trade of these products through international standards coordination and cross-linking. Governments could also coordinate their testing and certification requirements to ensure that a CO₂U product certified within one country will not need to be recertified

(leading to additional expense and delay) to enter another country's market.

Product labeling

Labels indicating the environmental qualities of products can increase demand for those products.¹⁶ In fields such as building energy efficiency, carbon neutrality, forests and fisheries, many private voluntary organizations define criteria for such labels. Such organizations often evaluate whether individual products meet those criteria as well.¹⁷ Many governments do the same. Prominent examples include the U.S. Energy Star and Energy Guide programs, the Japanese Energy Efficiency Label program, and the EU Energy Labeling Directive.

Two related strategies in this area could help increase demand for CO₂U products. First, products could be labelled to indicate the presence of captured CO₂. Second, existing labeling schemes could be modified to give credit for the use of CO₂ in a way that reduces life cycle emissions. Governments are well-positioned to launch such programs with the attention they attract, the resources they command and prior experience in this area. Any consumer-facing product with the potential for CO₂U could qualify. Leading candidates may include coatings, adhesives, sealants and related plastics products, as well as CO₂-based fuels. Governments could also work with voluntary labeling programs such as LEED to include credit for buildings that use CO₂U-based construction materials.

¹ See Sir Nicholas Stern, Stern Review on the Economics of Climate Change (2006) http://webarchive.nationalarchives.gov.uk/+/http://www.hm-treasury.gov.uk/sternreview_index.htm. See also Alison Benjamin, "Stern: climate change a market failure" *Guardian* (November 29, 2007) (quoting Sir Nicholas Stern – "Climate change is a result of the greatest market failure the world has seen") <https://www.theguardian.com/environment/2007/nov/29/climatechange.carbonemissions>

² See Robert Stavins, "Repairing the R&D Market Failure," *Environmental Forum* (Jan/Feb 2011) https://scholar.harvard.edu/files/stavins/files/column_40.pdf; Kenneth Gillingham and James Sweeney, "Market Failure and the Structure of Externalities" (July 2008) http://environment.yale.edu/gillingham/GillinghamSweeney_MktFailureStructureExternalities_proof.pdf

³ See <http://mission-innovation.net/our-work/baseline-and-doubling-plans/>

⁴ See Mission Innovation, Carbon Capture Innovation Challenge -- <http://mission-innovation.net/our-work/innovation-challenges/carbon-capture-challenge/>

⁵ Department of Energy Invests \$4.8 Million in Projects to Advance Beneficial Use of CO₂ (August 10, 2017) <https://energy.gov/fe/articles/department-energy-invests-48-million-projects-advance-beneficial-use-co2>

⁶ SCOT Project, EU-ETS to Incentivise CO₂ Utilization? <http://www.scotproject.org/images/Briefing%20paper%20EU%20ETS%20final.pdf>

⁷ FUTURE Act at 45Q(f)(2) <https://www.congress.gov/bill/115th-congress/senate-bill/1535/text>

⁸ See Tom Kenning, "Revision to 'single most important policy' to drive solar ready for approval," *PV Tech* (November 9, 2015) -- <https://www.pv-tech.org/news/intersolar-india-revision-to-single-most-important-policy-todrive-solar-re>

⁹ See generally David Gerard and Lester Lave, "Implementing Technology-Forcing Regulations," *Technological Forecasting and Social Change* (2005) <http://faculty.lawrence.edu/gerardd/wpcontent/uploads/sites/9/2014/02/18-TFSC-Gerard-Lave.pdf>

¹⁰ USDOE, A Review of the CO₂ Pipeline Infrastructure in the U.S. (April 21, 2015) at p.1 https://energy.gov/sites/prod/files/2015/04/f22/QER%20Analysis%20-%20A%20Review%20of%20the%20CO2%20Pipeline%20Infrastructure%20in%20the%20U.S._0.pdf; Global CCS Institute, CO₂ Pipeline Infrastructure (January 2014)

http://ieaghg.org/docs/General_Docs/Reports/2013-18.pdf; Linde Group

http://www.the-lindegroupe.com/en/clean_technology/clean_technology_portfolio/co2_applications/greenhouse_supply/index.html; CO₂ Europipe <http://www.co2europipe.eu/>

¹¹ Michael Barnard, "Climate Capture is Expensive Because of Physics," *Clean Technica* (January 19, 2016) <https://cleantechica.com/2016/01/19/carbon-capture-expensive-physics/>

¹² Esteban Ortiz-Ospina and Max Roser, "Public Spending" (2017) <https://ourworldindata.org/public-spending/>

¹³ See, e.g. "Comprehensive Procurement Guidelines for Construction Products", U.S. EPA website.

¹⁴ “Biofuels are included in latest U.S. Navy fuel procurement”, U.S. Energy Information Administration (July 25, 2014)

¹⁵ FUTURE Act at 45Q(f)(2) -- <https://www.congress.gov/bill/115th-congress/senate-bill/1535/text>

¹⁶ See Jo Bowman, “Green Branding” (March 2009) http://www.wipo.int/wipo_magazine/en/2009/02/article_0011.html; Jenny Chin-Hwa et al., “Will American consumers pay more for eco-friendly labeled canned tuna?” (May 2017) <http://www.sciencedirect.com/science/article/pii/S0308597X16304894>

¹⁷ See Ecolabel Index <http://www.ecolabelindex.com/ecolabels/?st=country,us>

Chapter 8:

Findings and Recommendations

Key findings

CO2U can be an important tool for achieving a wide set of policy objectives. These include stimulating and revitalizing industries, creating jobs and delivering environmental benefits (notably climate benefits).

Some of the most intriguing applications of CO2U are in early developmental stages. These include novel methods of converting CO₂ into chemicals, fuels and long-lived products. These appear to have the potential to displace carbon-intensive products in large volume with relatively modest material and energy costs.

With a strengthened and expanded innovation agenda, CO2U could deliver significant benefits in each of the three sectors discussed in this report. This conclusion is based on potential climate impacts, market values and technical improvements (based on thermodynamic and engineering limits), as well as the R&D needed to make many products cost-competitive.

More work is needed on life cycle analyses. For many CO2U applications, key data sets are needed for accurate and precise estimates of carbon reductions through LCA. Some existing methodologies require refinement for LCAs to undergird regulatory and policy decisions.

Similarly, many CO₂-based products lack standards or acceptance by standards organizations. While

existing market standards for some products such as ethylene and fuels may suffice, existing performance and compositional standards for many other products (including cements, carbon fiber, composites and new chemicals) will likely limit access to market for new products.

Key recommendations

Research, development and analysis

1. A sustained innovation agenda is needed to rapidly develop and improve CO2U processes and products. This will also accelerate their entry into commercial markets.
2. Part of that innovation agenda involves assessment and analysis of potential CO2U markets and potential climate benefits.
3. Dedicated and sustained R&D programs have repeatedly proved valuable in delivering large innovations. Multi-year planning and investment is required.
4. A wide range of potential R&D investments could be merited. Individual countries, states and regions can tailor investments around their existing infrastructure, institutions and markets. However, a set of scientific discipline-based basic and applied research appears broadly valuable, including materials science (especially catalysis focused on conversions) and reactive mineral physics. Investment in enabling technologies (like advanced manufacturing and supercomputing) also seems promising.



Cross-cutting issues

5. Life-cycle analysis (LCA) work on CO2U products should receive targeted and dedicated support to improve data and methodologies. In addition, governments and key stakeholders should create national and international working groups to better share results and standardize their outputs.
6. Similarly, technology developers, CO2U product vendors, and CO2U product users should work together to accelerate the development of national and international product standards. This should be done in partnership with national standards organizations (e.g. NIST in the U.S.) and the International Organization for Standardization (ISO).

Policy

7. Governments should recognize CO2U as a potential pathway to environmental and economic benefits, including climate benefits. They should consider including CO2U in formal climate commitments (e.g. NDCs within the Paris Agreement).
8. Governments should consider policy measures to support market entry of CO2U products. These could vary in form (e.g. tax credits, subsidies,

procurement mandates, etc.) but should be aimed at stimulating market adoption of CO2U.

9. Governments should expand a CO2U innovation agenda that includes increased R&D and related innovation.
10. Governments should provide regulatory clarity through the adoption and use of LCAs and product standards.

Final thoughts

As global markets evolve under the Paris Agreement and its successors, CO2U will likely play a larger role in providing opportunities for action. Although there is opportunity for the current technology set to improve and evolve, the progress to-date is noteworthy. Commercial interest in CO2U has grown dramatically in just the last two years. We see CO2U as a key component to a new carbon economy, in which CO₂ is considered a conventional feedstock for cradle-to-cradle, circular economy networks. These findings and recommendations will similarly evolve over time and change focus. The merit in future work will flow directly and indirectly from commitments made by leaders in industry, finance, government and innovation. Fortune will favor the experienced and the quick.

We are deeply grateful to the Ministry of Economy, Trade and Industry (METI) and New Energy and Industrial Technology Development Organization (NEDO), Japan, for launching and supporting the ICEF Innovation Roadmap Project of which this is a part.