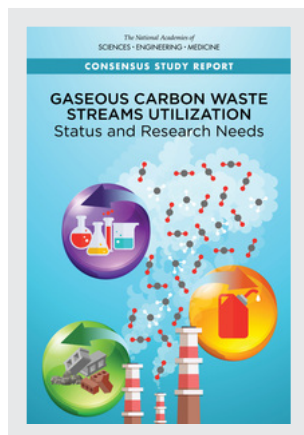## Gaseous Carbon Waste Streams Utilization: Status and Research Needs (2018)

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Gaseous Carbon Waste Streams Utilization: Status and Research Needs

Committee on Developing a Research Agenda for Utilization of
Gaseous Carbon Waste Streams

Board on Chemical Sciences and Technology

Division of Earth and Life Studies

A Consensus Study Report of

The National Academies of
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Preface

Global emissions of greenhouse gases to the atmosphere, caused by human activities, are now in excess of 35,000 teragrams (tg) per year, or roughly 5 tons per person per year. In countries with advanced economies, like the United States, emissions per capita are larger, in excess of 15 tons per person per year. Reducing greenhouse gas emissions, to levels that are consistent with limiting the extent of global warming to less than a 2°C increase over pre-industrial temperatures, will require a variety of approaches. Some approaches, such as expanding the use of energy sources that have low greenhouse gas emissions, will prevent emissions. Other approaches involve capturing greenhouse gas emissions; however, capturing and permanently sequestering gigatons of waste gas per year is technically challenging and imposes costs. An alternative to sequestration is to find a productive use for captured greenhouse gases, primarily carbon dioxide and methane. The Committee on Developing a Research Agenda for Utilization of Gaseous Carbon Waste Streams examined the roadblocks to commercialization of technologies that could utilize captured greenhouse gases. These technologies are mostly in their infancy, but, if successful, could create greenhouse gas mitigation technologies that can be operated at little cost or even provide net economic value.

There are reasons to be optimistic. Already there are commercial technologies, operating at relatively small scale, that are or could be using waste gas as their raw materials. Additional fundamental research and process development could enable even more carbon utilization pathways operating at scales that could collectively approach a gigaton per year. Expanding carbon utilization to a gigaton scale, however, would require not just fundamental breakthroughs and process development but also the creation of enabling purification, transport, and other infrastructures.

In its report, the Committee on Developing a Research Agenda for Utilization of Gaseous Carbon Waste Streams identifies advances that could enable much more extensive carbon utilization. Addressing this complex and multifaceted task required a committee with a broad set of expertise, ranging from fundamental research to product and process commercialization, and from biotechnology to cement and concrete production. I thank the committee members, who gave generously of their time and effort and who both learned from and informed their fellow committee members. I also thank the National Academies of Sciences, Engineering, and Medicine staff who organized us and our report, improved our writing, and supported the committee's work in many other ways. Finally, I thank the reviewers, whose thoughtful comments improved the technical content and presentation of the report.

David T. Allen, Chair
Committee on Developing a Research Agenda for Utilization of Gaseous Carbon Waste Streams

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U.S. Department of Energy and **Shell**, which sponsored the study and provided valuable data to help address the statement of task. The committee would especially like to thank Joe Powell (Shell), Todd Anderson (Office of Biological and Envrionmental Reseacrch), Bruce Garrett (Office of Basic Energy Sciences), Zia Haq (Office of Energy Efficiency and Renewable Energy), and John Litynski (Office of Fossil Energy), who served as the Department's liaison to the committee and was effective in responding to the committee's requests for information.

Speakers and invited participants at the committee's data-gathering meetings. These individuals are listed here: Madhav Acharya, ARPA-E; Vahit Atakan, Solidia Technologies; Harry Atwater, California Institute of Technology; Kathy Ayers, Proton Onsite; Andrew Bardow, Aachen University; Abhoyjit Bhown, Electric Power Research Institute; Jean Bogner, University of Illinois, Chicago; Walter Breidenstein, GasTechno; Paula Carey, Carbon8; Steven Chu, Stanford University; Travis Cone, Sen. Capito; Bernard David, Global Carbon Dioxide Initiative; Heleen DeWever, BioRecover; Marcius Extavour, Carbon X-Prize; Liam Forsythe, Sen. Heitkamp; Aaron Goldner, Sen. Whitehouse; Christopher Gurtler, Covestro; John Hansen, Haldor Topsoe A/S; David Hazlebeck, Global Algae Innovations; Rich Helling, The Dow Chemical Company; Howard Herzog, Massachusetts Institute of Technology; Jennifer Holmgren, Lanztech; Elizabeth Horner, Sen. Barrasso; Hillary Hull, Environmental Defense Fund; Aqil Jamal, Aramco Performance Materials; Mark Jones, The Dow Chemical Company; Walter Leitner, Max Planck Institute for Chemical Energy; Stuart Licht, George Washington University; Sean Monkman, CarbonCure; Ah-Hyung Alissa Park, Columbia University; Bob Perciasepe, Center for Climate and Energy Solutions; Allison Pieja, Mango Materials; Phil Pienkos, National Renewable Energy Laboratory; Brian Sefton, Oakbio; Ómar Sigurbjörnsson, Carbon Recycling International; Steven Singer, Lawrence Berkeley National Laboratory; Tim Skone, National Energy Technology Laboratory; Eric Stangland, The Dow Chemical Company; and Ben Woolston, Massachusetts Institute of Technology.

Acknowledgment of Reviewers

This Consensus Study Report was reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise. The purpose of this independent review is to provide candid and critical comments that will assist the National Academies of Sciences, Engineering, and Medicine in making each published report as sound as possible and to ensure that it meets the institutional standards for quality, objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process.

We thank the following individuals for their review of this report:

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Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations of this report nor did they see the final draft before its release. The review of this report was overseen by **JOHN ANDERSON**, Illinois Institute of Technology, and **ELISABETH DRAKE**, Massachusetts Institute of Technology. They were responsible for making certain that an independent examination of this report was carried out in accordance with the standards of the National Academies and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the National Academies.

Contents

Summary

Globally, human activities release approximately 35,000 teragrams (Tg) (million metric tons [MMT]) of carbon dioxide and 320 Tg (MMT) of methane into the atmosphere each year. As researchers and policy makers search for strategies to mitigate the buildup of these greenhouse gases, increasing attention has turned to the capture of gaseous carbon waste. Once captured, the gaseous carbon waste can either be geologically sequestered or put to productive use. Both options have costs, but utilization offers the opportunity for benefits from the use of the material. Carbon utilization technologies, as referred to in this report, convert gaseous carbon waste feedstocks (carbon dioxide or methane) into valuable products such as fuels, construction materials, plastics, and other useful products. These technologies have the potential to transform waste streams into resources, reduce greenhouse gas emissions, and in some cases generate positive economic returns.

Only a small fraction of the carbon dioxide and methane emitted each year is currently being captured and used. Most carbon utilization technologies are in their infancy. The Committee on Developing a Research Agenda for Utilization of Gaseous Carbon Waste Streams was convened by the National Academies of Science, Engineering, and Medicine at the request of the U.S. Department of Energy, and Shell to assess research and development needs relevant to understanding and improving the commercial viability of carbon utilization technologies (see Box S-1).

The report defines a research agenda to address the principal challenges associated with commercializing carbon utilization technologies. The report also identifies improvements needed in tools used for evaluating the economic and environmental attributes of carbon utilization technologies. Because an overarching goal of carbon utilization is to curb the accumulation of greenhouse gases in the atmosphere, the study focuses on technologies that have the potential to utilize gaseous carbon waste with a net reduction in greenhouse gas emissions. The report assumes that large volumes of gaseous carbon waste, especially carbon dioxide, will continue to be generated in the coming decades through continued use of fossil fuels. While the study considers

utilization technologies for both carbon dioxide and methane, the larger focus is on carbon dioxide.[1] The report is intended to help inform decision making surrounding the development and deployment of carbon utilization technologies under a variety of circumstances, whether motivated by a goal to improve processes for making carbon-based products, to generate revenue, or to achieve environmental goals.

Box S-1

Statement of Task

The National Academies of Sciences, Engineering, and Medicine will convene an ad hoc committee to conduct a comprehensive assessment of future research and development needs for carbon utilization. In particular, it will focus on the research and development needed for commercialization of technologies that can transform carbon waste streams into products such as chemicals, fuels, polymers, and/or aggregates at a reasonable cost and a net life-cycle reduction of greenhouse (GHG) emissions to the atmosphere. The committee will write a report that will:

1. Assess the global status and progress of carbon utilization technologies (both chemical and biological) in practice today that utilize waste carbon (including carbon dioxide, methane, and biogas) from power generation, biofuels production, and other industrial processes.

2. Identify emerging technologies and approaches for carbon utilization that show promise for scale-up, demonstration, deployment, and commercialization.

3. Analyze the factors associated with making technologies viable at a commercial scale, including carbon waste stream availability, economics, market capacity, energy and life-cycle requirements, scale, and other factors.

4. Develop a set of criteria to assess the extent to which the utilization technology addresses the factors identified in Task 3 and apply the criteria to technologies identified in Task 2.

5. Assess the major technical challenges associated with increasing the commercial viability of carbon reuse technologies and identify the research and development questions that will address those challenges.

6. Assess current research efforts, including basic, applied, engineering, and computational, that are addressing these challenges and identify gaps in the current research portfolio.

7. Develop a comprehensive research agenda that addresses both long- and short-term research needs and opportunities.

The report will provide guidance to research sponsors, as well as research communities in academia and industry regarding key challenges needed to advance the science and engineering required to enable carbon utilization at a commercial scale. The report will not include recommendations related to funding, government organization, or policy issues.

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[1] Methane is emitted in far lower quantities than carbon dioxide and is, without chemical transformation, useful as a fuel and as a chemical feedstock. Capture and reuse of methane waste gas as a fuel are relatively mature technologies, so the potential impact of development of methane utilization technologies, beyond direct capture and use as a fuel, is limited. Carbon dioxide, on the other hand, makes up a far larger share of overall greenhouse gas emissions and, once captured, generally requires chemical transformation for use. Most technologies for utilizing carbon dioxide are at a low level of maturity, suggesting carbon dioxide utilization technologies have both a larger potential for greenhouse gas mitigation and a greater need for research and development.

OVERARCHING FINDINGS

Previous assessments have concluded that in excess of one billion tons of carbon per year (roughly 3.6 billion tons of carbon dioxide >10 percent of current global anthropogenic carbon dioxide emissions) could feasibly be utilized within the next several decades if certain technological advancements are achieved and if economic and policy drivers are put in place. While the eventual scale of carbon utilization will be determined by a variety of technical, economic and policy drivers, over multiple decades, carbon utilization technologies could be instrumental in achieving a "circular carbon economy" in which waste is converted into resources, such as by capturing the products of hydrocarbon combustion and converting them back into hydrocarbon fuels. In the context of an envisioned economy based largely on solar and wind power inputs with no net carbon emissions, such technologies could enable hydrocarbon use while dramatically curbing greenhouse gas emissions.

Finding 1: Carbon utilization technologies have a role to play in future carbon management and the circular carbon economy.

Finding 2: To play a meaningful role in carbon management, carbon utilization needs to be done at scale. The scale of carbon waste utilization will depend on the pace of technology development and future energy, market, and regulatory landscapes.

Broadly, carbon dioxide utilization can be categorized into three main pathways: mineral carbonation to produce construction materials, chemical conversion to produce chemicals and fuels, and biological conversion to produce chemicals and fuels. Methane utilization pathways include chemical and biological conversion to produce chemicals and fuels, as well as the direct use of methane as a fuel.

Mineralization processes transform carbon dioxide into mineral carbonates, which can be used to make concrete and cement. Because these building materials are used at enormous scale and have product lifetimes that span decades, mineral carbonation represents a significant opportunity for long-term carbon sequestration in addition to being an opportunity for carbon utilization. A variety of processes that use carbon dioxide in the production of concrete and cement are already operating at limited commercial scales.

Chemical and biological carbon utilization processes transform carbon dioxide and methane into carbon-containing materials such as fuels, polymers, commodity chemicals, and fine chemicals. Some processes that use waste carbon dioxide or methane to produce high-value chemicals are already operating commercially (e.g., methanol, dimethyl ether, and polymers). In addition, some technologies that use waste carbon dioxide or methane to produce higher-volume, lower-margin chemicals have also begun to be operated commercially, though current operations are generally dependent on locally available, low-cost, nontransportable energy resources or feedstocks, so they are not currently scalable in every location.

Finding 3: Pathways for carbon dioxide utilization include mineral carbonation, chemical utilization, and biological utilization. Pathways for methane utilization include chemical utilization, biological utilization, and direct use as fuel. These pathways involve multiple scales of operation, are at various stages of maturity, and require different energy inputs, feedstocks, and infrastructures.

Gaseous waste streams can contain contaminants such as hydrogen sulfide, sulfur dioxide, nitrogen oxides, siloxanes, and other species. Often these contaminants pose barriers to the utilization of carbon dioxide or methane in these waste gases. As a result, cost-effective methods to separate contaminants from and clean gaseous waste will be important enabling technologies for carbon utilization. Additional enabling technologies, resources, and infrastructures may be particularly important for efficiently converting carbon dioxide into useful products. For example, low-cost, low-carbon sources of energy or energy-carrying components (hydrogen, heat, or electricity) are needed to utilize carbon dioxide at large scale with zero or net negative greenhouse gas emissions. Finally, there is often a mismatch between the locations where such energy sources are available and the locations and magnitudes of emitted carbon streams, necessitating transportation or co-location infrastructures to bring energy and waste gases together for processing.

Finding 4: Enabling technologies, resources, and infrastructures to remove waste gas contaminants provide necessary inputs of energy or reactive gases, and transport resources may be required for operation of carbon utilization technologies at scale.

At all stages of development from fundamental research to commercialization, researchers, technology developers, and policy makers evaluate technologies to make investment decisions. To compare the potential commercial viability of carbon utilization technologies, it is necessary to identify the factors that are crucial for marketplace success.

Finding 5: Like all technologies, a comprehensive evaluation of carbon utilization technologies would include evaluation at various maturity levels based on economic, market, regulatory, and environmental factors. Because carbon utilization technologies utilize waste streams and may involve social or regulatory barriers and incentives as well as disruptive change to energy and material manufacturers, there are unique facets to carbon utilization evaluation.

Table S-1 summarizes key factors to consider when evaluating carbon utilization technologies. Many of these factors, such as economic value, scale, and market penetration, are shared with any new technology. Other factors are specific to the context of gaseous carbon waste streams. While the criteria presented in Table S-1 provide a framework for evaluating

technologies, they can be applied in different ways depending on the evaluator's needs and the technology being assessed.

TABLE S-1 Factors to consider when comparing carbon utilization technologies, and associated criteria for evaluating those factors.

Factors	Criteria
Economic value	• Is the production cost of the carbon utilization–derived product competitive with the production cost of its immediate competitors in the market? • Would a company earn a sufficient internal rate of return from producing the carbon waste–derived product?
Scale, market capacity, and market penetration	• In what volumes is the product currently made through conventional means? • What is the potential market capacity of the analogous carbon-derived product? • Would the carbon waste–derived product be expected to achieve substantial market penetration within years, or would it take decades?
Control of external factors associated with the technology	• Does the producer of the technology have nearly full control of the value chain, or only a small portion of it?
Unintended outcomes and consequences	• Could the technology cause large market disruptions that affect areas such as land and water use patterns, chemical industry structures, or fuel usage patterns?
Availability and suitability of waste stream	• Is a sufficient quantity of carbon waste available at the required quality to produce the product at a cost that enables competitive market pricing? • Would changes in the carbon waste stream cause substantial changes in yield or purity of the product?
Risks associated with the use of waste as a feedstock	• Is the product subject to regulatory constraints relevant to the use of a waste feedstock in its production? • Would contamination in the product pose a threat to human health?
Life-cycle greenhouse gas reductions	• Are the life-cycle greenhouse gas emissions, water consumption, and air pollutant emissions of the carbon utilization–derived product advantageous compared to the same or functionally equivalent product produced conventionally? • What is the total potential for carbon uptake into the product, given the product's market potential and the amount of waste carbon incorporated per unit mass produced? • Will carbon be stored in the product for the short term (less than 1 year), medium term (up to a decade), or long term (decades)?

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Evaluating the factors and criteria outlined in Table S-1 requires tools and methods such as life-cycle assessment and technoeconomic analysis. However, many existing life-cycle assessments and technoeconomic analyses for waste carbon utilization processes and products are not sufficiently transparent, consistent, or accessible to allow for easy comparison of the unique features of carbon utilization technologies.

Finding 6: Current reported technology assessments, such as life-cycle assessment and technoeconomic analysis, frequently do not provide the needed level of transparency, consistency, and accessibility. Advances in technology evaluation tools would need to take place in parallel with the development of carbon utilization technologies.

A RESEARCH AGENDA FOR CARBON UTILIZATION

A comprehensive research agenda is needed to advance a wide range of carbon utilization technologies suitable for utilizing various carbon waste streams, incorporating enabling technologies and resources, and producing a variety of carbon-based products. In order to generate economic value while reducing greenhouse gas emissions, research is needed to address knowledge gaps throughout the carbon utilization landscape (Figure S-1). While some research needs are specific to the particular utilization technologies, others are cross-cutting, including research needs related to carbon inputs, process system improvement, catalytic technologies, and tools for evaluating utilization technologies.

Finding 7: A robust carbon utilization technology portfolio includes high-volume and high-value products, as well as products or processes that utilize resources available at low cost regionally or temporally, infrastructure, and feedstocks. Development of such a portfolio will require a broad range of research and technology advances.

Recommendation 1: In order to realize potential benefits including improved energy and resource efficiency, creation of valuable industrial products, and mitigation of greenhouse gas emissions, the U.S. government and the private sector should implement a multifaceted, multiscale research agenda to create and improve technologies for waste gas utilization.

Specifically, the U.S. government and the private sector should support:

- Research and development in carbon utilization technologies to develop pathways for making valuable products and to remove technical barriers to waste stream utilization;
- The development of new life-cycle assessment and technoeconomic tools and benchmark assessments that will enable consistent and transparent evaluation of carbon utilization technologies; and

- The development of enabling technologies and resources such as low- or zero-carbon hydrogen and electricity generation technologies to advance the development of carbon utilization technologies with a net life-cycle reduction of greenhouse gas emissions.

FIGURE S-1 The carbon utilization systems for both (a) carbon dioxide waste streams and (b) methane waste streams. Carbon waste gas streams enter each system on the left. Enabling technologies and resources are implemented as required. Chemical and biological utilization processes transform waste gas streams into products such as chemicals and fuels. In the case of CO_2 waste streams, the process of mineral carbonation can be utilized to produce products such as construction materials. The product lives extend into the short and long term for both systems, ultimately resulting in carbon emissions into the atmosphere or long-term storage, respectively. Collection and reuse of products as shown in (a) lead to a circular carbon economy for those recycled gases. The shaded box illustrates the system boundary for technoeconomic and life-cycle assessments, as well as for assessing the economic value that can be developed through the various aspects of carbon utilization.

Areas of focus, priority research needs, and relevant research goals are summarized in Table S-2. Research needs are discussed in greater detail in Chapter 11.

TABLE S-2 Key research needs to promote the development of a robust carbon utilization portfolio.

Area of Focus	Key Needs	Relevant Research Goals
Research Needs Related to Carbon Inputs		
Waste streams	Gaseous carbon waste mapping	Research is needed to map the detailed compositions and magnitudes of gaseous carbon waste streams, with particular attention to co-emitted species that could either hinder or enhance carbon utilization processes. This could increase opportunities for matching waste streams with appropriate utilization processes.
Research Needs Related to Utilization Processes		
Mineralization of carbon dioxide	Controlling carbonation reactions	Research is needed to understand the fundamental chemical features that control the relative rates of carbonation and hydration. This could lead to improved selection of alkaline solids and reaction conditions.
	Process design	Research is needed to integrate mineralization processes with existing carbon dioxide capture technologies. This could lead to increased process performance and ensure optimal carbon dioxide conversion rates and energy use efficiencies.
	Accelerating carbonation and crystal growth	Research is needed to develop additives for enhanced carbon dioxide solubility or structure-directing agents that accelerate particle growth. This could accelerate carbonation reactions such as crystal growth rates in solution beyond what is achieved simply by increasing the pH.
	Green synthesis routes for alkaline reactants	Research is needed to develop energy- and carbon dioxide–efficient pathways and processes for producing alkaline solids that can be readily carbonated and do not require high-temperature activation. This could lead to energy and carbon dioxide efficient pathways.

Area of Focus	Key Needs	Relevant Research Goals
	Structure-property relationships	Research is needed to develop physical and instrumental assessment methods, improved modeling, and performance-based criteria for product properties. This could improve predictions of structure-property relations and increase the durability, viability, and acceptance of carbonated solids.
	Analytical and characterization tools	Research is needed to develop new analytical tools for studying carbonation reactions in dense and viscous suspensions, as well as the evolution of microstructure across length scales. This could lead to new scientific tools to characterize mineralization technologies.
	Construction methodologies	Research is needed to develop new material formulations with novel properties and to advance the use of additive manufacturing to construct components with superior strength-to-weight ratio, optimized topology, and more complex geometries compared to what can be made with existing construction methods. This could enable new categories of carbon utilization products.
Chemical conversion of carbon dioxide	Chemical catalysis	Research is needed to improve existing catalysts or discover entirely new catalysts. In addition to the usual performance metrics (activity, selectivity, and durability), special attention should be given to designing catalysts that tolerate the impurities present in carbon dioxide–containing waste streams to avoid costly and energy-intensive carbon dioxide purifications.
	Avoiding stoichiometric additives	Research is needed to find ways to avoid stoichiometric additives that are not integrated into products, or to identify additives that are easily regenerated. This could lead to processes that could be used, with limited waste generation, for commodity chemical or fuel production.
	Integrating catalysis and reactor design	Research is needed to integrate catalysts with the most efficient reactor including the identification of factors that affect catalyst performance at synthetically relevant rates. This could accelerate the development of carbon

Area of Focus	Key Needs	Relevant Research Goals
		dioxide conversion processes that are relevant at the commercial scale.
	Pathways to new products	Research is needed to develop processes that produce nontraditional targets, especially those with carbon-carbon bonds. This could transform processes for producing a wide range of chemicals and could create new markets.
	Coupling oxidation and reduction reactions	Research is needed to combine carbon dioxide reduction with the oxidation of substrates from other waste streams (e.g., agricultural or biomass waste). This could open new pathways to reduce the cost of carbon dioxide conversion and create multiple high-value products.
	System engineering and reactor design	Research is needed to develop reactor technologies that are tailored to the demands of carbon dioxide conversion processes. For example, reactors that allow for very efficient removal of products that are formed at low conversion for thermodynamic reasons would be beneficial. For electrochemical conversions, reactors that optimize single-pass conversion would mitigate the costs of product separation. Systems that integrate carbon dioxide capture with conversion should also be explored to minimize the steps required for waste gas valorization.
Biological conversion of carbon dioxide	Bioreactor and cultivation optimization	Research is needed to improve bioreactor system design for efficient carbon dioxide solvation, mass transfer, dewatering and harvesting, and management and recycling of water and nutrients. This may include development of better computational and modeling tools for optimizing cultivation processes. Advancement of nonphotosynthetic methods may require novel bioreactor design in order to incorporate new feedstocks or hybrid fermentative systems. This could improve culture-monitoring technologies and facilitate scale-up of utilization.
	Analytical and monitoring tools	Research is needed to improve culture-monitoring technologies. This could facilitate scale-up.

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Area of Focus	Key Needs	Relevant Research Goals
	Genome scale modeling and improvement of metabolic efficiency	Research is needed to develop and improve methods for in-depth computational modeling, genetic manipulation, biochemical validation, and fermentative demonstration. This could improve metabolic flux, including carbon dioxide uptake and incorporation, photosynthetic efficiency, metabolic streamlining, and product accumulation.
	Bioprospecting	Research is needed to accelerate the identification and characterization of organisms or biological systems with unique attributes such as carbon dioxide uptake, various product profiles, photosynthetic efficiency, and environmental tolerance. This could enhance the ability to produce target products in diverse geographic locations.
	Valorization of coproducts	Research is needed to develop feed and food uses for coproducts of biological conversion, including studies in product safety and acceptability. This could improve the efficiency of energy and materials use and increase the economic value of biological conversion technologies.
	Genetic tools	Research is needed to enhance engineering of photosynthetic and nonphotosynthetic organisms, including expansion of tools for genetic incorporation, selectable markers, promoter elements, protein folding and stability, and posttranslational control. This could improve efficiency and rates of biomass production and selective product formation.
	Pathways to new products	Research is needed to identify biological pathways to produce nontraditional products and new products for unmet needs in commodity and specialty chemicals. This could expand the portfolio of products made via carbon utilization.
Research Needs for Evaluating Utilization Technologies		
Life-cycle assessment	Life-cycle assessment benchmarking	Research is needed to develop benchmark life-cycle assessments of waste gas generation, waste gas cleanup, waste gas transport, electricity inputs, hydrogen inputs,

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Area of Focus	Key Needs	Relevant Research Goals
		and other enabling technologies to facilitate consistent and transparent assessments of the net greenhouse gas emissions of carbon utilization technologies. These benchmark assessments should include multiple environmental attributes of carbon utilization life cycles, such as greenhouse gas emissions, water use, air emissions, and materials use. This could lead to more consistent assessments of technologies.
	Life-cycle assessment (LCA) of emerging waste carbon utilization technologies	Research is needed to learn from transparent life-cycle assessments of emerging technologies, taking into account a system boundary that includes waste gas capture and cleanup, the conversion process, use phase, and end-of-life considerations. Although LCA results for emerging technologies will undoubtedly evolve, LCA at this early stage will help guide research toward activities that will heighten energy and environmental benefits.
	Assessment of disruptive change	Research is needed to develop life-cycle assessment tools that move beyond assessing marginal changes in existing, static systems and address disruptive changes resulting from large-scale carbon utilization. This will provide tools for assessing disruptive changes necessary for performing consequential LCAs of carbon capture and utilization systems.
Technoeconomic analysis	Technoeconomic assessment benchmarking	Research is needed to develop standardized, transparent inputs and assumptions for technoeconomic analysis implemented for carbon utilization. This could lead to more consistent assessments of technologies.
	Entrepreneurial research hubs	Research is needed to elucidate issues such as social and behavioral acceptance and understanding of commercialization needs. Entrepreneurial research hubs could support links between fundamental research and market needs.
	Pilot plant facilities	Research is needed at pilot plant facilities to reduce risks involved in the commercialization of new technologies. This could facilitate the development of technologies beyond the laboratory scale.

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Area of Focus	Key Needs	Relevant Research Goals
	Advanced testing	Research is needed to develop predictive accelerated aging evaluation methodologies for mineral carbonation. Such models would help de-risk technologies and streamline their introduction into conservative market applications where extensive performance data are needed to establish codes for use.

Cross-cutting

Process system improvement: Examples include more efficient techniques for mass transport or solvation of gaseous waste, better process-monitoring techniques, process intensification and optimization, integration of carbon utilization processes with carbon capture technologies, integration of catalysis research with reactor design, and techniques for managing and recycling inputs or products to minimize waste.

Improved catalysis: Examples include catalysts for accelerating carbonation based on control and distributions of surface sites on catalysts (for mineralization), catalysts that use sustainable raw materials (for chemical utilization), catalysts for hydrogenation of lipid extracts (for biological utilization), and catalytic technologies that reduce the cost and complexity of product recovery, as well as reduce toxicity to the host organism (for electrocatalysis).

INTEGRATION WITH CURRENT RESEARCH ACTIVITIES

Research and development that is directly or indirectly relevant to carbon utilization is supported, directed, and performed in industry, academia, government, and the nonprofit sector. In the United States, research that impacts carbon utilization and enabling technologies is scattered throughout various federal research portfolios, including fundamental and applied research and development grant mechanisms administered by the Department of Energy, Department of Defense, and the National Science Foundation, as well as through private-sector research and development programs.

> **Finding 8: Numerous research efforts relevant to advancing carbon utilization are under way both in the United States and abroad, supported by both public and private funding. Coordination and communication among existing carbon utilization research programs can lead to more rapid technology advancements.**

Recommendation 2: The U.S. federal science agencies should coordinate carbon utilization research and development efforts with private-sector activities in the United States and with international activities in the private and public sectors. Support for carbon utilization research and development should include technologies throughout different stages of maturity, from fundamental research through to commercialization, and evaluate them using a consistent framework of economic and environmental criteria.

CONCLUDING REMARKS

This research agenda reflects the priority needs that would enable the advancement of a wide range of carbon utilization technologies suitable for utilizing various carbon waste streams to produce a variety of carbon-based products. Incorporating enabling technologies and resources and integrating better coordination among the current research efforts will advance the progress being made in carbon utilization, which may play a significant role in carbon management even if fossil fuels are largely replaced by low-emissions energy sources.

1

Introduction

Waste streams containing carbon dioxide, methane, and biogas[1] represent large flows of emissions into the atmosphere. These emissions, which have risen sharply over the past several centuries due to anthropogenic activities, are a hazard primarily due to their greenhouse gas effect. Carbon capture, utilization, and sequestration technologies may play a critical role in reducing global greenhouse gas emissions. Carbon capture paired with sequestration for reducing CO_2 emissions from large point sources has received considerable attention as one approach to greenhouse gas mitigation. More recently, strategies that pair carbon capture with utilization have been receiving increased attention from researchers and policy makers as an alternative path for captured carbon dioxide or methane.

Carbon utilization is based on the concept that gaseous carbon waste streams can have value as feedstocks for producing fuels, construction materials, plastics, or other useful materials. For the purposes of this report, carbon utilization is defined as the manufacture of valuable products from a gaseous carbon waste feedstock (carbon dioxide and methane) that results in a net reduction of greenhouse gases emitted to the atmosphere.[2] This value may be captured by different actors and may represent economic value stemming from production and use of the product made from the carbon waste stream, or it may represent the value of reducing emissions that results from carbon utilization. The ultimate value and extent of carbon utilization will depend on future technology, economics, and policy drivers. This report identifies key scientific and technological barriers to carbon utilization and the factors that will influence the extent of carbon utilization and suggests a research agenda that would further enable carbon utilization.

The sources and types of gaseous carbon waste are illustrated in Figure 1-1 and discussed in more detail in Chapter 2. In the United States, carbon dioxide emissions are primarily due to fossil fuel combustion while methane emissions stem primarily from oil and gas production, landfills, livestock, and manure (NASEM, 2018). A third source of gaseous carbon waste, biogas, contains both carbon dioxide and methane and is generated by the degradation of biomass in the absence of oxygen.

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[1] Biogas is a mixture of methane, carbon dioxide, and other trace species. It is generated by anaerobic biological processes, often in landfills or sewage treatment facilities.
[2] The calculation of net greenhouse gas emissions is described in Chapter 8.
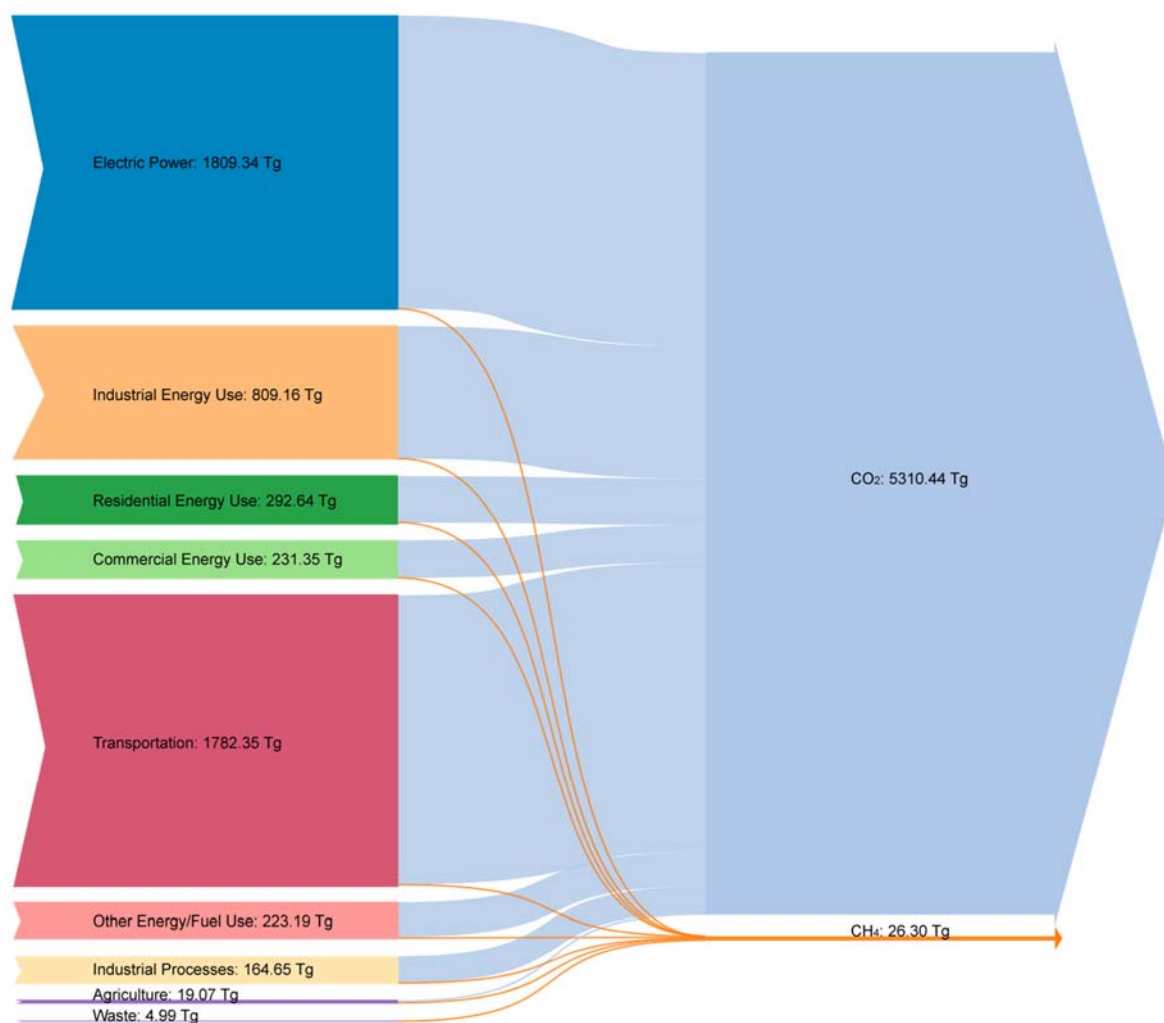
FIGURE 1-1 U.S. carbon dioxide and methane emissions sources by mass (in Tg) in 2016. Data from EPA, 2018.

Mitigating greenhouse gas (GHG) emissions is and will be an important goal for many who are exploring carbon utilization technology development and implementation. There are many scenarios for mitigating GHG emissions to the atmosphere, ranging from decarbonization of energy and other economic sectors to carbon capture with sequestration and/or utilization. The long-term mitigation impact of carbon utilization technologies will depend on the life-cycle emissions from production through use of the product, through the fate of the carbon at end of product use. Key aspects determining the mitigation potential of carbon utilization technologies and resulting products include the greenhouse gas emissions associated with product production, the volume of carbon embedded in the product (depending on the size of the product market and amount of carbon incorporated), the product lifetime during use, and the ultimate fate of the carbon in the product at end of use. Different products and processes will have different resulting

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mitigation impacts, and carbon waste stream utilization may be pursued for reasons other than long-term carbon mitigation.

Currently, capture of carbon waste gases is limited, with 45 large-scale carbon dioxide capture projects operating with a total capture capacity of 80 million tons per annum, globally (Global CCS Institute, 2015). The majority of the captured gases are sequestered, and the utilization of gaseous carbon waste is limited to niche applications. There are many scenarios for how carbon flows will operate in the future, including scenarios with varying mixes of deep decarbonization of energy and other sectors, as well as scenarios with carbon capture and/or utilization. Some envision a much larger role for carbon utilization in the future management of carbon emissions. For example, Shell's latest energy-system scenario, Sky, depicts the potential achievement of net-negative emissions by 2100 through a combination of large-scale (11 Gt/yr) capture and geologic storage of carbon dioxide and even larger scale removal of carbon dioxide with photosynthesis (26 Gt/yr). The Sky scenario relies on a complex combination of reinforcing drivers, accelerated by society, markets, and governments and follows three distinct routes (see Figure 1-2). In such a scenario, carbon wastes could become inputs to a cyclic industrial system that transforms the wastes into useful products through biological and chemical processes.
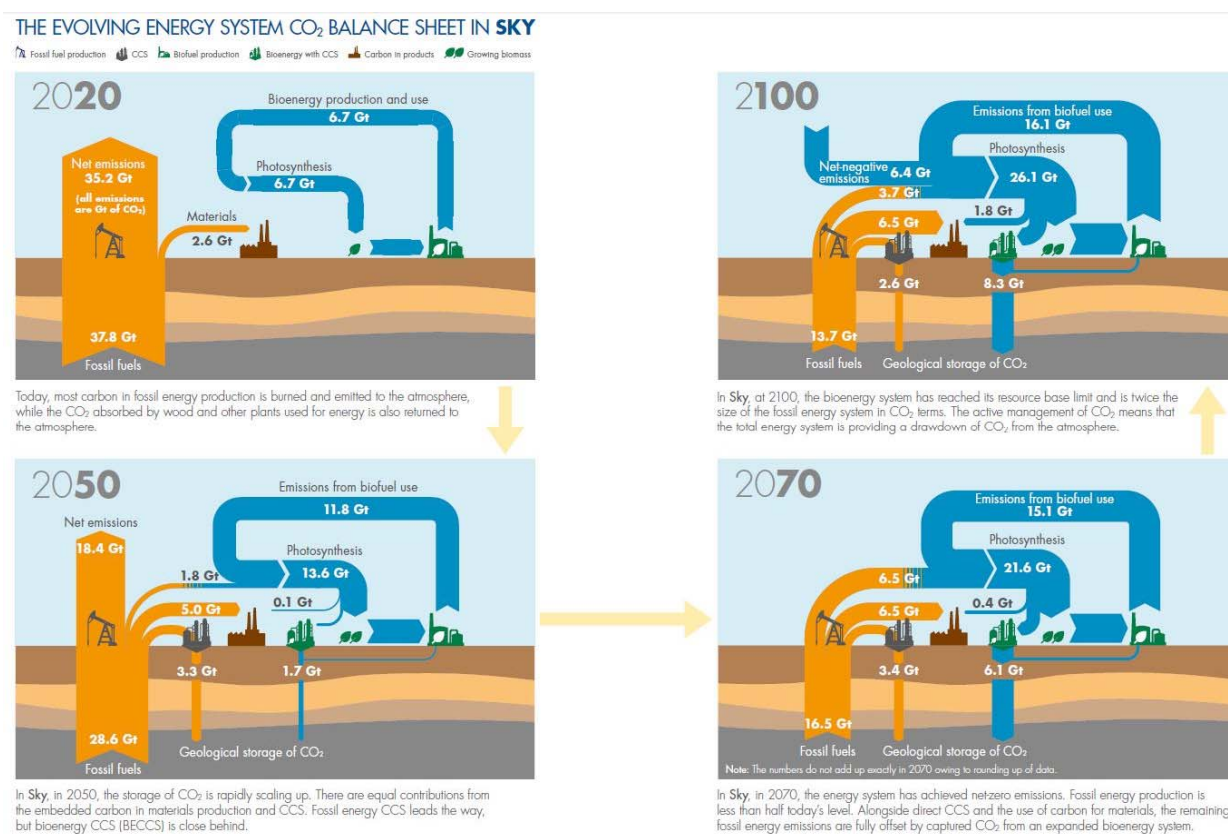
FIGURE 1-2 Shell's "Sky" scenario for achieving net-negative emissions by 2100. SOURCE: Shell International, 2018.

STUDY CHARGE

At the request of the U.S. Department of Energy (DOE) and Shell, the National Academies of Sciences, Engineering, and Medicine (the Academies) assembled an ad hoc committee to assess the economics, benefits, risks, scale, energy, and life-cycle requirements for carbon utilization technologies and develop a detailed research agenda to increase the technical and commercial viability of carbon utilization (Box 1-1).

Box 1-1

Statement of Task

The National Academies of Sciences, Engineering, and Medicine will convene an ad hoc committee to conduct a comprehensive assessment of future research and development needs for carbon utilization. In particular, it will focus on the research and development needed for commercialization of technologies that can transform carbon waste streams into products such as chemicals, fuels, polymers, and/or aggregates at a reasonable cost and a net life-cycle reduction of greenhouse (GHG) emissions to the atmosphere. The committee will write a report that will:

1. Assess the global status and progress of carbon utilization technologies (both chemical and biological) in practice today that utilize waste carbon (including carbon dioxide, methane, and biogas) from power generation, biofuels production, and other industrial processes.

2. Identify emerging technologies and approaches for carbon utilization that show promise for scale-up, demonstration, deployment, and commercialization.

3. Analyze the factors associated with making technologies viable at a commercial scale, including carbon waste stream availability, economics, market capacity, energy and life-cycle requirements, scale, and other factors.

4. Develop a set of criteria to assess the extent to which the utilization technology addresses the factors identified in Task 3 and apply the criteria to technologies identified in Task 2.

5. Assess the major technical challenges associated with increasing the commercial viability of carbon reuse technologies and identify the research and development questions that will address those challenges.

6. Assess current research efforts, including basic, applied, engineering, and computational, that are addressing these challenges and identify gaps in the current research portfolio.

7. Develop a comprehensive research agenda that addresses both long- and short-term research needs and opportunities.

The report will provide guidance to research sponsors, as well as research communities in academia and industry regarding key challenges needed to advance the science and engineering required to enable carbon utilization at a commercial scale. The report will not include recommendations related to funding, government organization, or policy issues.

STUDY APPROACH

In addressing its charge, the committee limited the scope of the study by carbon waste stream, type of carbon use, and geography. Only carbon waste streams that contain carbon dioxide, methane, or biogas were considered, and the committee focused on the utilization of only these

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components of gaseous waste streams. While gaseous waste streams commonly contain other gases and particles, these other constituents were only considered insofar as they impact the utilization of carbon dioxide, methane, or biogas. The committee did not focus extensively on the capture of carbon dioxide and methane, as that is being examined by a parallel study under way at the National Academies (Box 1-2). Carbon utilization technologies that are already mature or do not chemically transform carbon dioxide or methane into products or materials were excluded from the study.

Box 1-2

Study relationship to Committee on Developing a Research Agenda for Carbon Dioxide Removal and Reliable Sequestration

In recognition of the role that carbon dioxide removal and sequestration technologies can play in meeting greenhouse gas reduction goals, the National Academies convened an ad hoc committee to evaluate the state of science and viability of technologies for removing carbon dioxide from the atmosphere. The resulting report, *Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration* (NRC, 2015), recommended investments in research and development for technologies that remove carbon dioxide from the atmosphere. Building on this report, the National Academies convened two committees, one to identify research needs for carbon dioxide removal from the atmosphere and sequestration, and one to study utilization of concentrated carbon waste gas streams. The Committee on Developing a Research Agenda for Carbon Dioxide Removal and Reliable Sequestration assessed the benefits, risks, and "sustainable scale potential" for atmospheric carbon dioxide removal and sequestration approaches and defined the essential components of a research and development program, including estimates of the program's cost and potential impact. The Committee on Developing a Research Agenda for Utilization of Gaseous Carbon Waste Streams developed a research agenda for conversion of concentrated waste gas streams of carbon dioxide, methane, and biogas as a feedstock into commercially valuable products. The committee surveyed the current landscape of carbon utilization technologies and identified key factors and criteria associated with making these technologies commercially viable. Together, the two committees' reports provide an assessment of research needs and opportunities to remove and utilize gaseous carbon.

The study focuses on advancing carbon utilization within the United States but recognizes that U.S. carbon utilization takes place within a larger global context. For example, it is assumed that waste gas feedstocks and other inputs may come from other countries, and that international market demand plays a role in the commercial viability of products produced in the United States. It is also assumed that domestic utilization technologies would take advantage of state-of-the-art research and technologies developed anywhere; as a result, the committee's information-gathering process included input from speakers involved in carbon utilization research and development outside the United States.

Although the economic and environmental evaluation of carbon utilization technologies is discussed in Chapters 8 and 9, the committee did not attempt to conduct detailed economic and environmental evaluations of any particular technology. The committee's focus was on identifying scientific and technological barriers to carbon utilization (Chapters 3-6 and 11) and on identifying factors and criteria that should be used to evaluate the commercialization potential of various technologies (Chapter 10). The prioritized research needs for waste carbon utilization range from fundamental research to research needed for commercialization. The committee attempted to

identify broad progressions of research, starting with fundamental research, proceeding to proof-of-concept activities at the bench scale, pilot scale, and demonstration scale, and concluding with research needed at near-commercial stages. The boundaries between the stages are not distinct.

To support its deliberations, the committee gathered information from experts and stakeholders from government agencies, industry (including trade associations), and academia. A list of those experts and stakeholders may be found in the Acknowledgments. Information about current utilization technologies at all levels of technology readiness was provided to the committee during several data-gathering meetings and follow-up communications. The committee also gathered information from public documents, including the scientific literature and government reports.

The committee structured its activities by examining carbon dioxide utilization, methane utilization (including biogas), and enabling technologies, resources, and analyses. Each of these segments of the carbon utilization system is described below.

CARBON DIOXIDE UTILIZATION

A wide variety of potential uses have been identified for carbon dioxide waste, as illustrated in Figure 1-3. Carbon dioxide has been used for decades in enhanced oil recovery, as a refrigerant, as an extractive solvent, and as an additive in food and beverage products; as technologically mature processes that do not involve chemical transformations, these uses were outside the study scope.[3] Instead, the committee focused on emerging carbon dioxide utilization waste stream technologies that offer the promise of a net reduction in greenhouse gas emissions, including the mineral carbonation to produce construction materials and the chemical or biological conversion of carbon dioxide to fuels and chemicals.

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[3] CO_2 is already used in commercial processes, both in its pure form and as a feedstock in the synthesis of bulk chemicals such as urea. In the pure form, CO_2 is presently used in the food industry with applications that vary from carbonation of drinks to accelerated production of greenhouse tomatoes. Likewise, bulk CO_2 is also used as solvents in processes such as dry cleaning of fabric and decaffeination. CO_2 has also been used in enhanced oil and gas recovery by pumping it under near-critical or supercritical conditions into oil fields where conventional recovery has become uneconomical or impractical.

Liquid Fuels
Fertilizer
Polymers
Secondary Chemicals

Mineral Carbonation
• Carbonates

Chemical Conversion
• Alcohols
• Acids
• Hydrocarbons
• Polymer Precursors
• Carbon Nanotubes
• Carbon Monoxide

Biological Conversion
• Green Algae
• Cyanobacteria
• Chemolithotrophs
• Bio-electrochemical systems

Captured CO_2

Extractant
• Flavors/Fragrances
• Decaffeination

Refrigerant
• Refrigeration
• Dry Ice

Food/Products
• Carbonated Beverages

Fire Suppression
• Fire Extinguishers

Enhanced Fuel Recovery
• EOR
• EGR
• ECBM

Inerting Agent
• Blanket products
• Protect carbon powder
• Shield gas in welding

Miscellaneous
• Injected into metal castings
• Added to medical O2 as a respiratory stimulant
• Aerosol can propellant
• Dry ice pellets used for sand blasting
• Red mud carbonation

Oil
Gas

FIGURE 1-3 Schematic illustrating the variety of potential uses for carbon dioxide after it has been captured. Blue lines and boxes indicate the committee's areas of focus. SOURCE: Modified from DOE.[4]

A number of studies have attempted to estimate the market for carbon utilization products and one published study has reported the future market could be as high as $800 billion by 2030, utilizing 7 billion metric tons of carbon dioxide per year (CO_2 Sciences, Inc., 2016). Three broad categories of carbon utilization were considered by the Committee:

1. *Conversion to inorganic products (mineral carbonation).* This process converts stable CO_2 into an even more stable form of carbon, typically a carbonate, which can be used to produce

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[4] https://www.netl.doe.gov/research/coal/carbon-storage/research-and-development/co2-utilization. Accessed on October 10,2018

construction materials such as concrete. Mineralization involves reaction of minerals (mostly calcium or magnesium silicates) with CO_2 to give inert carbonates. The reaction to form carbonates itself requires no energy inputs and actually releases heat, although significant energy is typically required to generate the requisite feed minerals. The current bottleneck, however, for viable mineral carbonation processes on an industrial scale is the reaction rate of carbonation. Additionally, new formulations of materials such as concrete will require testing and property validation before being accepted by users and regulators for the market.

2. *Chemical conversion.* It is possible to use CO_2 for the production of fuels and chemicals by reacting it with other molecules and/or providing electrochemical, photochemical, or thermal energy. These conversions require catalysts to overcome kinetic barriers. Because carbon in CO_2 is in its most highly oxidized form, many of the resulting reactions are reductions, either through the addition of hydrogen or electrons. Catalysts are critical not only for making the transformation possible, but also for reducing the energy inputs to (ideally) the minimum amount dictated by the thermodynamics of the transformation, and discovery of appropriate catalysts and development of energy-efficient processes are current bottlenecks.

3. *Biological conversion.* Biological conversion involves using photosynthetic and other metabolic processes inherent to plants, algae, bacteria, and fungi to produce higher-value chemicals. Several factors have expanded the repertoire of bio-based products that can be synthesized directly from CO_2, including the large number of CO_2-utlizing microorganisms; genetic modification of microorganisms, and tailoring enzymatic/protein properties through protein engineering. Bioconversion has a large range of potential uses in the development of commercial products, including various biofuels, chemicals, and fertilizers. However, bioconversion rates and scalability remain challenges.

These carbon utilization approaches are discussed in detail in Chapters 3-5.

METHANE UTILIZATION

Although carbon dioxide waste gas utilization is a main focus of this report, methane also serves as a source of carbon for making products, as described in Figure 1-4. The two gases differ in physical and chemical properties and in the locations, magnitudes, and properties of the waste gas streams (see Chapter 2). Carbon dioxide is fundamentally a low-value, low-energy waste gas, which is often available in large quantities in single locations. Methane, in contrast, is a high-value, high-energy molecule. Because of its high value and high energy of combustion, methane as a waste gas is only available in low quantities, or with intermittent flows. If methane is available as a waste gas, chemical uses of the waste gas must compete against the value of methane as a fuel, limiting possible nonfuel utilization pathways.

Methane from waste gases, including biogas, can be collected and used directly as a fuel. Direct use of methane from waste gases, without chemical modification, is a relatively mature

technology and was considered by the committee only in the context of improved gas cleaning operations that would make these energy recovery processes more economical. In addition to direct use as fuel, methane in waste gases can be used as a feedstock in chemical and fuel manufacturing technologies. Some chemical pathways that use gaseous methane to make liquid fuels (e.g., Fischer-Tropsch synthesis) are relatively mature technologies and were outside the study scope. Instead, the committee focused on pathways for using methane to produce fuels and chemicals that are at an earlier stage of research and development.
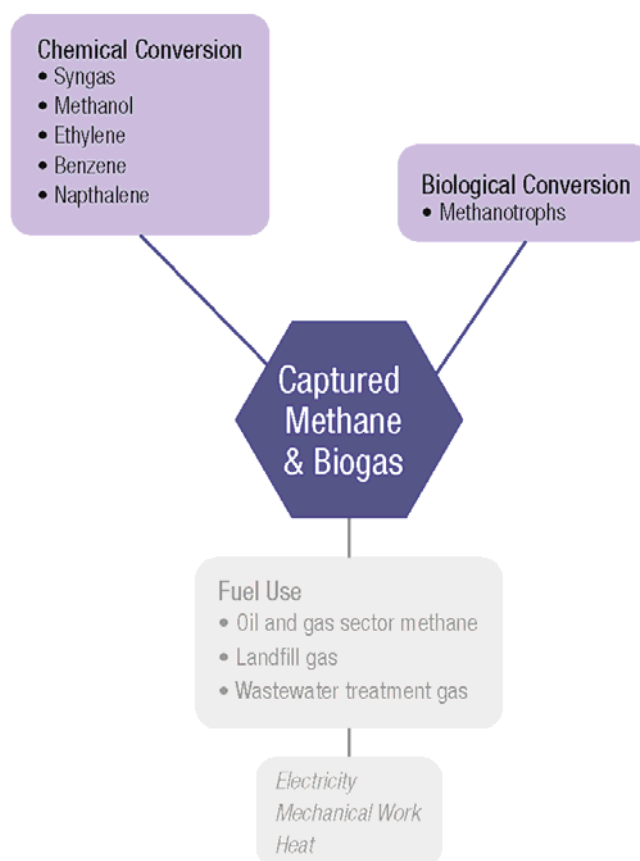
FIGURE 1-4 Schematic illustrating the variety of potential uses for methane after it has been captured. Blue lines and boxes indicate the committee's areas of focus.

Like carbon dioxide, methane and biogas can also be converted to products such as fuels, fine chemicals, polymers, and other materials through chemical or biological means. However, because methane is so chemically different from carbon dioxide, different utilization pathways and technologies are generally needed for the utilization of methane or biogas versus carbon dioxide. Technologies and research needs for the utilization of methane waste and biogas are discussed in Chapter 6.

ENABLING RESOURCES, TECHNOLOGIES, AND ANALYSES

Enabling resources, technologies, and analyses are required to accomplish carbon utilization at scale with a net reduction in greenhouse gas emissions. For example, carbon dioxide utilization typically requires hydrogen, heat, or electricity; these resources will need to come from renewable or other low-carbon sources to achieve a net reduction in carbon emissions. Enabling technologies such as separation and purification, processing, and transportation are also vital for developing efficient and low-emissions utilization systems. Spatial disconnects between the sources of the waste streams, the sources of the enabling resources, and the facilities where valuable products are being produced can necessitate improved infrastructure and process design solutions. These and other enabling resources and technologies are discussed in Chapter 7.

Life-cycle assessment (LCA), discussed in Chapter 8, is a critical tool to evaluate the total energy requirements and environmental impacts involved in producing chemicals, fuels, construction materials, and polymers from waste carbon feedstocks. LCA is particularly relevant for evaluating carbon utilization technologies when a goal of the technology is to achieve a net reduction in greenhouse gas emissions.

Determining the technical and economic viability of a new technology is initiated through a technoeconomic analysis (TEA). Components considered in a TEA, discussed in Chapter 9, include defining a conceptual process design, performing a feasibility assessment through material and energy balances in combination with economic projections, examining the thermodynamic and kinetic models governing the technology process, estimating capital and operating costs, and classifying the technology according to its technical readiness. Key considerations for carbon waste gas stream utilization include cost, quantity, and purity of the waste stream; costs and carbon footprints of other reactants and inputs; product quality and marketability; and availability of capital with an appropriate risk tolerance. A TEA may also consider how the evaluation will change over time and across geographies as conditions vary. However, determining the commercialization potential of a new product or process requires consideration of factors beyond the technology and economic viability such as market-focused components and legal components. Market-focused components to be considered include an evaluation of the end market size and competitiveness and the perception of the technology offering, while legal components to be considered include consideration of regulatory issues, intellectual property, and standards and norms in the market of interest.

Chapter 10 describes factors and criteria that can be used to evaluate the commercialization potential of carbon dioxide and methane utilization technologies and presents illustrative cases demonstrating the use of those factors and criteria.

Chapter 11 provides a comprehensive research agenda for removing technical barriers and developing viable pathways for carbon dioxide and methane utilization.

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2

Gaseous Carbon Waste Resources

Approximately 10,000 teragrams (Tg) of waste gas carbon is emitted globally each year (see Figure 2-1), representing a large volume of potential inputs for carbon utilization technologies. However, these gaseous waste streams are heterogeneous in their composition, are emitted from a wide range of geographically distributed sources, and are not always easily transported from their sources to locations where they can be processed. This heterogeneity poses challenges for carbon utilization. As shown in Table 2-1, sources of carbon dioxide range from highly concentrated by-products of chemical manufacturing to relatively dilute flue gas streams from power plants with contaminants that can be problematic for carbon utilization technologies. Methane in waste gas ranges from widespread biogas from waste treatment and landfill facilities, containing challenging contaminants, to sparse coal mine venting of dilute methane in air. This chapter describes the sources, compositions, and geographical distributions of carbon dioxide and methane in gaseous waste streams and explores how those characteristics relate to the specifications for carbon utilization feedstocks. This chapter will also attempt to distinguish between those sources of methane in waste gas that are more likely to be directly reused as fuel rather than chemically transformed through carbon utilization technologies.

FIGURE 2-1 Growth in global carbon emissions, 1900-2014. Data from Boden et al., 2017.

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TABLE 2-1 Gaseous waste streams containing carbon dioxide and methane in the United States in 2016. SOURCE: EPA, 2018.

Waste Gas	Approximate Magnitude in the United States	Composition	Chemical Species Also Found in Waste Gas
Carbon dioxide from ammonia manufacture	12.2 Tg (MMT)	> 98% CO_2	Hydrogen, water, carbon monoxide, nitrogen
Carbon dioxide from fossil fuel combustion	4,966 Tg (MMT)	12-15% CO_2	Nitrogen, nitrogen oxides, particulates, sulfur oxides
Carbon dioxide from cement, iron/steel, and glass production	82.9 Tg (MMT)	20-35% CO_2	Carbon monoxide, particulates, nitrogen and nitrogen oxides, sulfur oxides
Carbon dioxide from natural gas production	25.5 Tg (MMT)	3-4% CO_2	Water vapor
Methane from oil and gas	1.54 Tg (38.6 MMT CO_2e)	50-95% CH_4	Ethane and other light alkanes as the other dominant species
Methane from landfill gas	4.3 Tg (107.7 MMT CO_2e)	50% CH_4 50% CO_2	
Methane from digestor gas	0.36 Tg (8.9 MMT CO_2e)	70% CH_4 30% CO_2	
Methane from coal mine vents	2.2 Tg (53.8 MMT CO_2e)	1-10% CH_4	

NOTE: CO_2e: carbon dioxide equivalent.

CHARACTERIZATION OF CARBON WASTE STREAMS

Carbon utilization technologies focus on conversion of two major carbon resources—carbon dioxide and methane—into useful products. Although some gaseous waste streams contain both of these carbon resources, in general carbon dioxide and methane waste gases differ in terms of their physical and chemical properties and in the locations, magnitudes, and other properties of the waste gas streams. The following sections describe key characteristics of carbon dioxide– and methane-containing waste streams.

Carbon Dioxide Waste Streams

Global emissions of carbon dioxide waste caused by human activities, primarily fossil fuel combustion, have been increasing rapidly. Counter to the global trend, carbon dioxide emissions have been decreasing in the United States, from an estimated peak of 5.38 billion metric tons of carbon dioxide in 2004 (after accounting for uptake by forestry and land use change) to an estimated 4.56 billion metric tons of carbon dioxide in 2016 (approximately 14 percent of the world total of 35 billion metric tons of carbon dioxide, or approximately 10,000 Tg of carbon) (EPA, 2018). Trends in carbon dioxide emissions result from long- and short-term drivers, including population and economic growth, market trends, technological changes, and fuel choices. Carbon dioxide emissions in the United States come almost exclusively from the combustion of carbonaceous fuels in five major sectors: electricity generation, transportation, industrial processes and fuel use, residential fuel use, and commercial fuel use (See Figure 2-2).

U.S. Environmental Protection Agency (2018). Inventory of U.S.
Greenhouse Gas Emissions and Sinks: 1990-2016
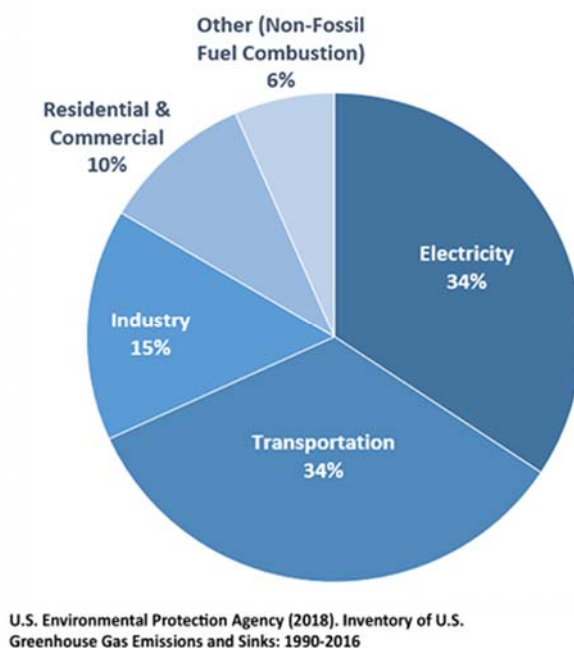
FIGURE 2-2 U.S. carbon dioxide emissions by source in 2016. SOURCE: EPA, 2018.

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Power Plants

About one-third of U.S. carbon dioxide emissions come from electric power plants that burn fossil fuels and generate waste gases at high rates. For example, a single 1,000-megawatt coal-fired power plant, operating at full capacity, generates approximately 1,000 tons of carbon dioxide per hour or roughly 9 Tg (million metric tons [MMT]) per year. U.S. power plant emissions totaled 1,800 Tg (MMT) in 2016 (EPA, 2018). Concentrations of carbon dioxide in the flue gases from electric power plants are typically in the range of 12 to 15 mol% for coal-fired plants and 3 to 4 mol% for natural gas powered plants (Songolzadeh et al., 2014). As shown in Figure 2-3, waste streams from power plants are geographically distributed throughout the United States and are disproportionately concentrated near major population centers. In addition to carbon dioxide, these waste gases can contain a variety of contaminants, including nitrogen oxides, sulfur oxides, heavy metals, fly ash, and other species.

GHGRP, 2016

Power Plants Sector Emissions (metric tons CO_2e)

- · <500,000
- · 500,000—2,000,000
- ● 2,000,000—5,000,000
- ● 5,000,000—10,000,000
- ● >10,000,000

Data Source: 2016 Greenhouse Gas Reporting Program
As of: 08/05/2017
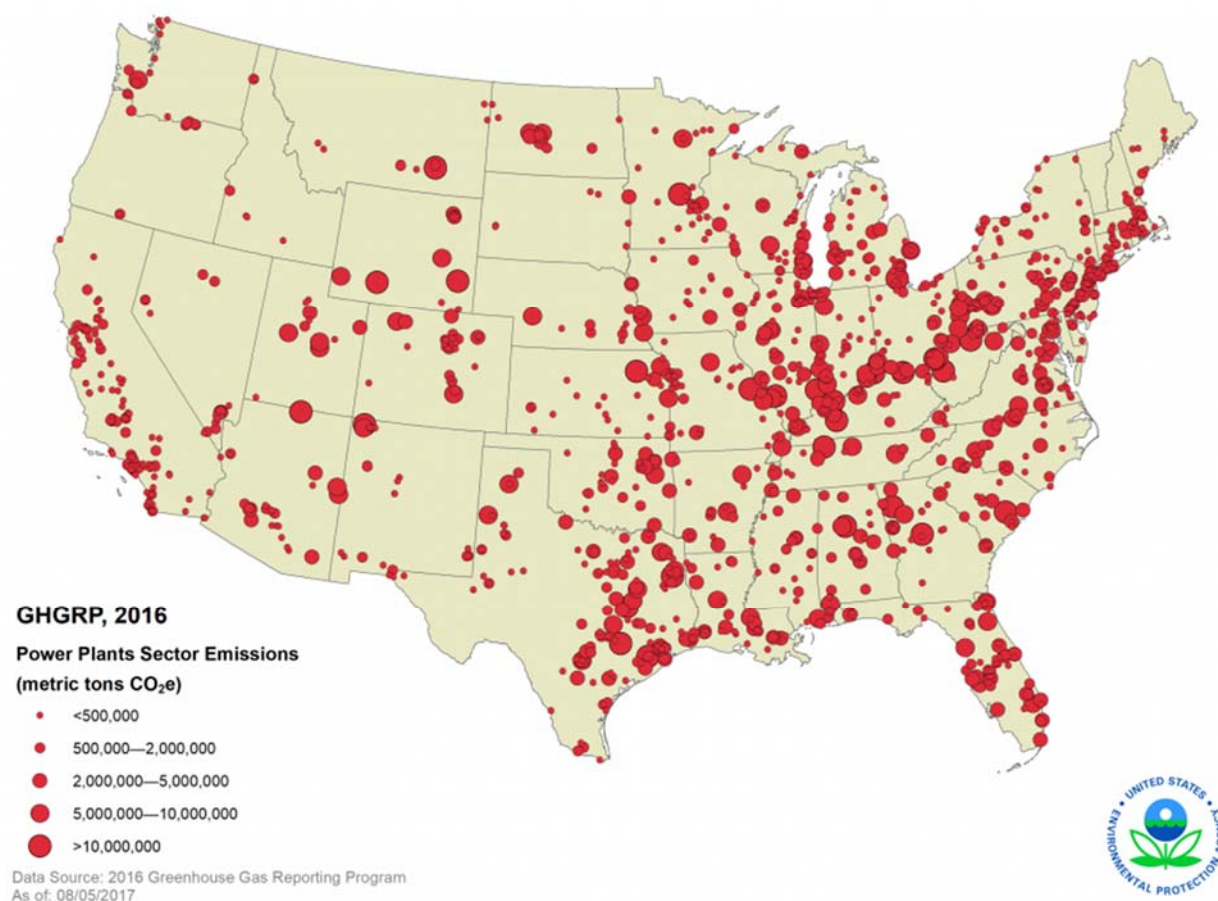
FIGURE 2-3 Greenhouse gas emissions from U.S. power plants in 2016. SOURCE: EPA, 2016a.

Manufacturing Facilities

In contrast to the waste streams from electric power plants, which are widely distributed, available in large volumes, and have variable levels of contaminants, manufacturing facilities can emit waste streams that are smaller in volume but contain higher concentrations of carbon dioxide and fewer contaminants. The chemical industry is the largest source of industrial CO_2 emissions in the United States (Figure 2-4). These include waste streams from hydrogen and ammonia manufacturing facilities, which produce particularly concentrated sources of CO_2. Another source of highly concentrated industrial CO_2 is from biofuel processing facilities, particularly ethanol fermentation plants. Cement, steel, and glass manufacturing facilities also emit significant volumes of carbon dioxide; in 2016 such facilities emitted 39.4, 1.2, and 6.9 Tg (MMT) of carbon dioxide, respectively. Cement production represents the second largest source of industrial carbon dioxide emissions in the United States. While emissions from glass production have stayed relatively constant over the past 15 years, emissions from steel production have decreased due to technological improvements and increased scrap streel utilization.
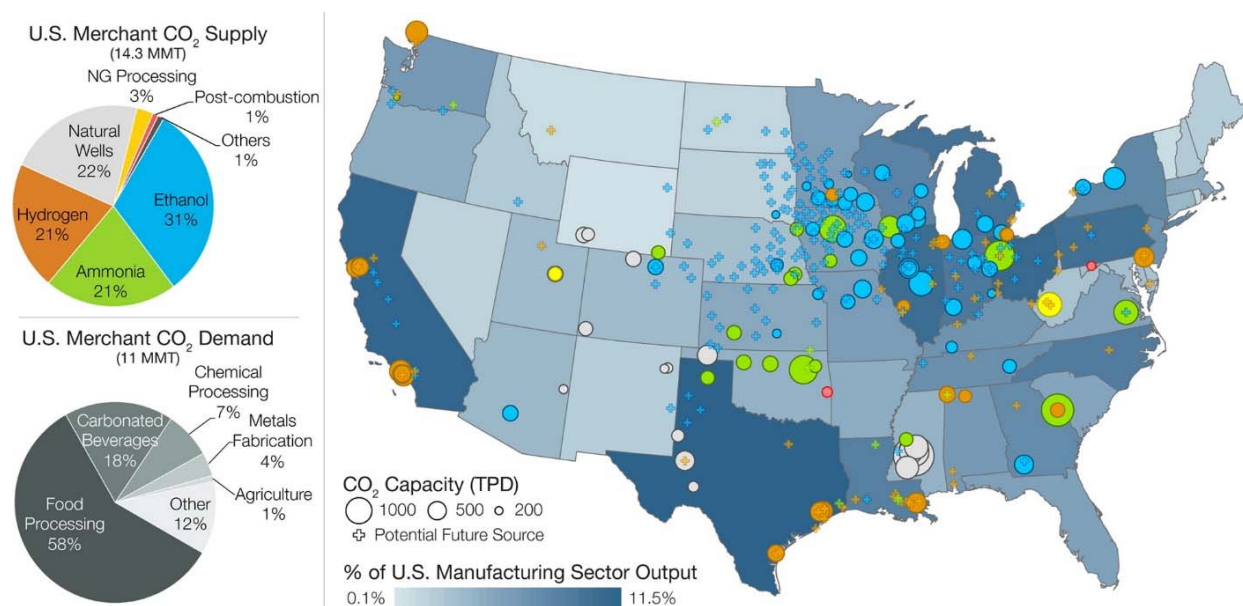
FIGURE 2-4 Map of merchant CO_2 supply and demand. Reprinted with permission from Supekar, S. D. and S. J. Skerlos. 2014. Market-Driven Emissions from Recovery of Carbon Dioxide Gas. Environmental Science & Technology. 48 (24), 14615-14623. doi: 10.1021/es503485z. Copyright 2014 American Chemical Society.

Methane Waste Streams

Carbon dioxide is fundamentally a low-value, low-energy waste gas that is often emitted in large flows from individual sources. Methane, by contrast, is a high-value, high-energy molecule that is emitted as waste in far lower quantities, often in intermittent flows. Chemical uses of methane-containing waste gases compete against the value of methane as a fuel, limiting possible utilization pathways.

Global annual emissions of methane to the atmosphere total approximately 558 Tg/yr (MMT/yr). Approximately 60 percent of these emissions are due to anthropogenic activities, dominated by fossil fuel production and use (105±28 Tg/yr) and agriculture and waste processing (188±54 Tg/yr) (NASEM, 2018). In the United States, which emitted approximately 26.3 Tg (MMT) of methane in 2016 (EPA, 2018), the dominant sources of methane as a waste gas are petroleum and natural gas systems, enteric fermentation (emissions by ruminant animals), manure emissions, landfills, wastewater treatment, and coal mining (Figure 2-5). Waste gas from landfills and wastewater treatment are referred to as biogas, since the methane is generated by microorganisms under anaerobic conditions.

Among the major categories of methane emission sources, a recent National Academies report characterized the degree of confidence in emission rates as high for coal-mining vent gases, as medium for enteric emissions and petroleum and natural gas systems, and as low for landfills and manure management (NASEM, 2018).

U.S. Environmental Protection Agency (2018). Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2016
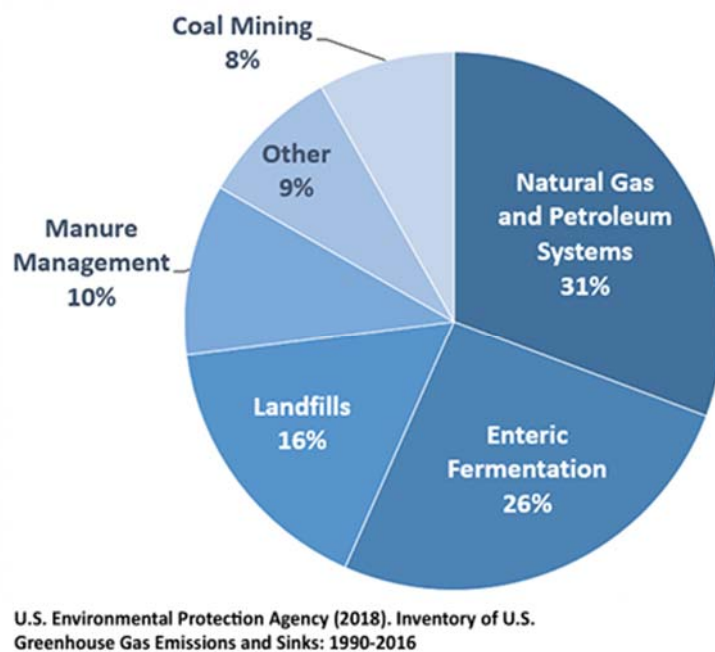
FIGURE 2-5 Methane emissions in the United States in 2016. SOURCE: EPA, 2018.

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In contrast to carbon dioxide, where large point source emissions are distributed throughout the United States, chemical uses of methane-containing waste gases may be much more limited by the dispersed and intermittent nature of methane waste gas sources. Even if captured, the value of methane as a fuel may limit possible nonfuel utilization pathways for methane. In order to identify which portions of the 26.3 Tg (MMT) of methane in waste gas in the United States might be available for nonfuel carbon utilization, a sector-by-sector analysis of emissions was performed by the committee. As described below, a large fraction of methane emissions in waste gas will face significant barriers to use as a feedstock for carbon utilization due to difficulties in capture, intermittency in emissions, or competition from direct reuse as fuel.

Oil and Natural Gas Production

Methane emissions from the natural gas supply chain have been estimated to be approximately 1.7 percent of total natural gas production, both globally (IEA, 2017) and in the United States (Littlefield, 2017). Alvarez et al. (2018) places the total at a higher level, approximately 2.3 percent of natural gas production, but there is general agreement on the nature of the major sources of emissions. Table 2-2 lists estimates of the emissions from the top five sources in the natural gas sector, which collectively account for approximately 4 Tg (MMT) of methane per year or about half of the estimated total emissions from the natural gas sector that appear in the methane inventory assembled by the U.S. Environmental Protection Agency.

TABLE 2-2 Total emissions and basis of emission estimation for the top five emission sources within the natural gas systems. SOURCE: EPA, 2018.

GHGI Emission Source	Sector	2016 Emissions (kiloton)
Gathering and boosting stations	Production	1955.1
Pneumatic controllers[a]	Production	1053.2
Transmission station total fugitive emissions	Transmission and storage	580.1
Gas engines (compressor exhaust vent)	Production	245.6
Engines (compressor exhaust in transmission)	Transmission and storage	253.6

[a] Devices used in petroleum and natural gas systems to regulate liquid levels, valves, and gas pressure. Controllers, powered by natural gas pressure when open, release methane (EPA, 2016b).

A variety of assessments have estimated the extent to which these emissions might be captured or reduced. For example, the International Energy Agency, in its special section on natural gas in the 2017 World Energy Outlook (IEA, 2017), estimated that approximately half of methane emissions associated with natural gas production could be reduced at a cost that could be justified based on the fuel value of the natural gas recovered or saved. Other analyses have made similar conclusions (ICF International, 2014, 2016). Many proposed strategies for methane emission reduction involve preventing, rather than utilizing, emissions. For example, among the largest sources of emissions in the natural gas supply chain are pneumatic controllers, which use gas pressure to open and close control valves, releasing methane as the controller operates. Natural gas can be replaced by compressed air to power pneumatic devices, eliminating this source of emissions. Methane emitted as a result of leaks and methane released as unburned fuel from compressors could also be prevented by sealing the leaks and improving the compressor engine performance. While such measures would prevent methane emissions, they do not fall within the scope of chemical utilization as defined in this report. Other sources of methane emissions in natural gas production may be less preventable but nonetheless have limited potential for carbon utilization processes, largely due to their intermittent nature. For example, emissions from compressor and pipeline blowdowns, as well as venting of wells to remove accumulated liquid, can lead to very large flow rates of methane (reaching approximately 1,000 kilograms per hour; Allen et al., 2015), but the events may be brief and infrequent, making utilization challenging.

Overall, the most consistent major source of methane emissions that is potentially available for utilization processes is vented or flared associated gas. Associated gas is natural gas that is co-produced with oil. In some production regions (e.g., the Bakken field in North Dakota), early development was focused on petroleum production, and the infrastructure necessary for delivering natural gas to markets was not initially available. In the absence of natural gas gathering and transmission infrastructure, some of the natural gas produced along with oil (associated gas) was vented or flared. Venting of associated gas has declined rapidly in the United States as natural gas gathering and transmission infrastructure is built into new production regions (EPA, 2017). Currently, approximately 0.2 percent of the 30 trillion cubic feet of natural gas production in the United States is flared. Allen et al. (2016) report a detailed analysis of flaring in upstream oil and gas operations in the United States and conclude that a majority of the flared gas is concentrated at a small number of locations. Associated gas flaring therefore represents the most consistent source of methane waste gas in the oil and gas sector that is available in relatively large volumes. This gas is typically in the range of 50 to 90 percent methane, with the remainder being ethane, propane, butanes, and other light hydrocarbons. Depending on the formation, the gas may contain also hydrogen sulfide or carbon dioxide.

Coal Mines

Underground coal mines are another source of methane emissions. In active mines, various types of forced ventilation shafts are used to prevent dangerous accumulation of methane, which can lead to explosions. In 2016 approximately 251 underground mines across the United States collectively emitted a total of 1.64 Tg (MMT) of methane, comparable to the amount flared in the oil and natural gas sector (EPA, 2018). This methane is available at ventilation shaft discharge points, where methane makes up about 1-10 percent of emitted gas, with mine shaft air comprising the rest. This source of methane remains active while underground mines are active; however, underground mining of coal has been decreasing in the United States, and, once a mine becomes inactive, emissions from venting decrease over time (NASEM, 2018). Therefore, while currently a relatively large-scale source of methane, this source of methane is generally projected to decrease going forward.

Enteric Fermentation and Manure

Another large category of methane emissions is enteric fermentation. Enteric fermentation emissions in the United States come primarily from beef and dairy cattle, ruminant animals that emit methane mainly via exhaled gases and eructation. Only about 2 percent is estimated to be due to flatulence (NASEM, 2018). Unless the animals are confined in an enclosure, it is difficult to collect these emissions for utilization. When confined to enclosures such as dairy barns, methane from enteric fermentation will be mixed with emissions from manure. Emissions from manure will depend on manure management practices, which vary widely. The most extensive methane production from manure management occurs when manure slurries are sent to anaerobic digesters. If the digester is enclosed, a gas stream consisting of approximately 30-60 percent methane can be recovered (EESI, 2017; Fulhage et al., 1993). The remainder of the gas stream can include ammonia, hydrogen sulfide, and a variety of organic compounds including organic sulfides, disulfides, C4 to C7 aldehydes, amines, quinoline, dimethylpyrazine, and organic acids, along with lesser amounts of C4 to C7 alcohols, ketones, aliphatic hydrocarbons, and aromatic compounds (NRC, 2003).

Landfills

In landfills, microorganisms digest buried wastes in anaerobic conditions, generating gaseous waste in relatively large quantities. Because this landfill gas consists primarily of methane and carbon dioxide, in roughly equal quantities, it has significant energy content. Energy recovery from landfill gases has been practiced for decades in the United States; however, the economic value of this waste gas utilization has been marginal, with landfill gas energy recovery becoming

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more or less prevalent as the prices of other fuels, most notably natural gas, vary over time. A challenge to the utilization of landfill gases as fuel is the potential for these waste streams to include trace contaminants such as various halogenated organic compounds, hydrogen sulfide, mercury-containing compounds, siloxanes, ketones, and sulfur-containing species (EPA, 1998, 2008).

Overall, roughly two-thirds of the 26.3 Tg/yr of methane in waste gas in the United States will face serious barriers to carbon utilization. The barriers are primarily related to the ability to capture the methane or the intermittency of the sources; however, the fuel value of methane will also potentially drive some emissions to be prevented rather than find use as a chemical feedstock. While some sources of carbon dioxide waste gases (e.g., transportation source) also face these challenges, fixed point sources of carbon dioxide emissions from power generation or other industrial applications provide volumes of waste carbon dioxide that are likely remain greater than the potential uses in carbon utilization for many decades

> **Finding 2-1** Waste gas streams containing carbon dioxide or methane are extensive but also heterogeneous. The chemical composition of contaminants of waste gases, difficulties in gas capture, and intermittency in waste gas flow can limit utilization opportunities.

MATCHING CARBON WASTE STREAMS WITH UTILIZATION PROCESSES: RESEARCH NEEDS

The carbon sources contained in waste streams are rarely available in pure form, and the composition of waste gas streams varies widely, depending on the source of the waste gas. Which chemical species found in gaseous carbon waste streams pose challenges to carbon utilization processes also depends on the utilization technologies to be used. Some carbon utilization processes require purified streams. For example, carbon dioxide used in food products and food processing has high purity requirements. On the other hand, some carbon utilization technologies can valorize species other than carbon dioxide and methane in waste gases, making the impurity of the waste gas stream a benefit. For example, Lanzatech[1] uses microbes that convert carbon-rich waste gases containing carbon monoxide, hydrogen, carbon dioxide, methane, and other species into a variety of products. The microbes use carbon monoxide as an energy source; this carbon monoxide would otherwise need to be treated as an air pollutant, and this avoided cost increases the economic benefit of the carbon utilization technology.

Because detailed characterizations of waste stream compositions are not widely available and the tolerance of carbon utilization processes for impure carbon dioxide and methane feeds is not generally known, it can be challenging to determine separation and purification requirements. In addition, most current carbon utilization activities take an opportunistic approach to accessing

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[1] See http://www.lanzatech.com/.

waste streams, rather than a systematic approach to match waste streams with the utilization processes for which they are best suited. Psarras et al. (2017) mapped potential industrial CO_2 sources with potential utilization locations to calculate transportation and other costs of utilization processes at different locations and with different concentration needs. A coordinated approach requires better integration between separation and purification targets and information about the waste stream and processes to be used.

A priority research area is:

Gaseous carbon waste characterization

Research is needed to map the detailed compositions and magnitudes of gaseous carbon waste streams, with particular attention to co-emitted species that could either hinder or enhance carbon utilization processes. This will increase opportunities for matching waste streams with appropriate utilization processes.

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3

Mineral Carbonation to Produce Construction Materials

Mineral carbonation processes use waste CO_2 to produce construction materials. Mineral carbonation offers an attractive route to CO_2 utilization because (1) solid carbonates, the main products of mineral carbonation reactions, are already used in construction materials markets; (2) the chemistry involved in making carbonates based on calcium (Ca) and magnesium (Mg) is well known; (3) carbonation can consume large amounts of CO_2 by chemically binding it into stable, long-lived mineral carbonates; and (4) the reaction of CO_2 with alkaline solids is thermodynamically favored, thereby needing little, if any, extrinsic energy. This chapter assesses the current state of research in mineral carbonation, highlights pathways to convert CO_2 to carbonates consisting of calcite $(CaCO_3)$, magnesite $(MgCO_3)$, or mixtures of the two (see Figure 3-1), and identifies market and environmental considerations relevant to the commercialization of mineral carbonation technologies.

Carbonates, commonly in a particulate or granular form, are predominately used in the production of cement and concrete, though they also find use in a variety of industrial applications, including in paper and food production.[1] Depending on their end use, carbonates may be formed as nominally pure compounds or as mixtures with silicates, aluminates, and/or ferritic compositions. Natural carbonates are available from mined geological sources such as limestone quarries. In mineral carbonation, synthetic carbonates are made by contacting alkaline solids, often in an aqueous suspension, with carbon dioxide[2] (Vance et al., 2015; Sanna et al., 2014). The conversion of CO_2, a low-energy molecule, into solid mineral carbonates is one of only a few thermodynamically favorable reactions involving CO_2 and can be accomplished at near-ambient temperatures. For this reason and because of the tremendous size of the construction materials market (more than 50 billion tons of material such as concrete and mineral aggregates are produced annually[3]), mineral carbonation is considered to be among the largest and most energy-efficient routes for CO_2 utilization. The market for construction materials produced through mineral carbonation using waste CO_2 is expected to be further bolstered by the growing demand for "green" buildings and construction materials, for example, to meet and exceed design

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[1] See https://pubchem.ncbi.nlm.nih.gov/compound/10112.

[2] An example carbonation (CO_2 mineralization) reaction involves the interaction of CO_2 with portlandite to produce calcite and water: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. The reaction is thermodynamically favored ($\Delta G = -74.61$ kJ/mol) and exothermic ($\Delta H = -68$ kJ/mol) and proceeds spontaneously under ambient conditions at relative humidities greater than 25 percent.

[3] See http://www.concreteconstruction.net/business/global-demand-for-construction-aggregates-to-exceed-48-billion-metric-tons-in-2015_o.

and construction standards such as LEED (Leadership in Energy and Environmental Design).[4]
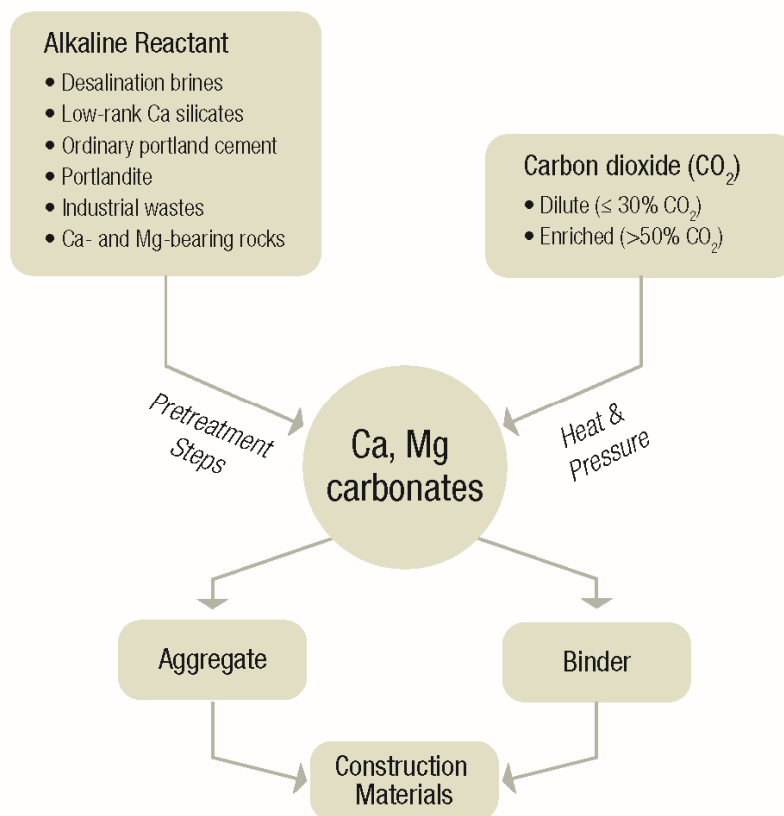
FIGURE 3-1 The process of mineral carbonation brings alkaline reactants into contact with dilute or enriched CO2 and results in the production of carbonate mineral aggregates, binding agents, and mixtures of the two that can be readily used as construction materials. The application of heat and pressure depends on the specific process and product requirements.

EMERGING TECHNOLOGIES FOR MINERAL CARBONATION

Mineral carbonation can be used to produce aggregates and binding agents suitable for use in construction materials. The process can involve a variety of approaches depending on the inputs used and the desired properties of the outputs. Some of these approaches are already employed commercially, suggesting the near-term potential for increased adoption of mineral carbonation in the large and growing construction materials market. More information on the existing commercial approaches is provided later in the

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[4] See https://new.usgbc.org/leed.

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chapter. However, a variety of factors influence the energy required and environmental impacts of these processes, which must be accounted for if mineral carbonation is to attain industrially relevant levels, thereby ensuring a net reduction in CO2 emissions.

Mineral Carbonation Products

The construction materials industry represents the primary market for products of mineral carbonation using waste CO2. Mineral carbonation can be used to make both aggregates and binding agents, which could potentially displace natural and existing synthetic sources of these important components of common construction materials.

Aggregates

Mineral aggregates, which range in size from micrometers to centimeters, are granular materials that form the dominant content of a concrete. By volume, mineral aggregates comprise roughly 60-80 percent of a typical concrete, with the rest consisting of a binding phase, or matrix. Currently, the vast majority of aggregates used globally are natural materials including sand, gravel and crushed rock, and other virgin materials mined from quarries, gravel pits, seabeds, and riverbeds. A smaller proportion are secondary and manufactured aggregates (Cresswell, 2007) including recycled concrete, byproducts from industrial processes (e.g., blast furnace slag), and mineral aggregates that are purpose manufactured for use in concrete (e.g., geosynthetic aggregate and carbonate-cemented aggregate; Colangelo and Cioffi, 2013). Globally, pressures on natural aggregate resources have increased as a result of growing restrictions on mining activities and the depletion of quality aggregate sources in proximity to urban areas. These and other factors have driven an increased emphasis on secondary and manufactured aggregates; for instance, roughly 10 percent of aggregate produced, by mass, in Europe today consists of recycled or manufactured material, an approach which is promoted by limited landfill capacities and high landfill use fees in the region (ECO-SERVE Network, 2004). Mineral carbonation is expected to represent a promising avenue for aggregate production, as long as the synthetic products are economical and meet relevant quality and performance standards.

Concrete

Concrete is the dominant material used in the construction of buildings and other infrastructure. It consists of a mixture of aggregates (primarily sand and stone), water, chemical additives, and cement. Cement is the binding agent in concrete; upon reaction

with water, cement forms a matrix that holds the solid components of concrete together, creating a synthetic rock that can be shaped as it hardens. Ordinary Portland cement (OPC), the most common type of cement, is produced from limestone, silica, clay, and iron compounds, along with other additives. While OPC has proved a strong and reliable building material over the past two centuries, its production and use have a large carbon footprint, generating approximately 0.7 tons[5] of CO_2 emissions per ton of cement produced and consumed globally.[6] These CO_2 emissions stem largely from the thermal decomposition of limestone (primarily $CaCO_3$) to lime (CaO) and from fuel burning to provide the heat required to drive the formation of clinker phases in the kiln, a foundational step of OPC production. While the construction and cement sector has significantly reduced the CO_2 impact of concrete production by improving kiln thermal efficiencies and combining cementitious materials such as fly ash and slags with OPC in the binder fraction (Snellings, 2016), these reductions have been more than offset by the global increase in cement consumption over the same period.

Concrete is most often used as ready-mix concrete or in the form of precast components. In the United States, ready-mix concrete, precast concrete, and concrete masonry comprise about 55, 25, and 15 percent of the overall concrete market, respectively.[7] The differences in these market segments are broadly operational. In the typical application of ready-mix concrete, a slurry of concrete is transported by truck to a construction site, where it is placed into formwork staged with reinforcing steel[8] and then allowed to harden into a structural component (i.e., floor, wall, beam, column, slab, etc.). Following hardening, the formwork is removed. In the case of precast concrete, a concrete slurry is cast into formwork or molds in the form of beams, columns, or slabs, often at a location far from construction sites. These components are then allowed to harden, following which the formwork is removed and the precast sections are transported to a construction site where they are assembled into buildings and infrastructure. Concrete is commonly classified by its compressive strength following 28 days of aging, which determines the load bearing capacity of a given concrete formulation and the types of structural or nonstructural components it may be used for.

Cement manufacturing plants are located in close proximity to the limestone quarries from which they draw their main feedstock, which are typically far from urban centers. Both limestone and cement are heavy, low-cost materials, and the cost of shipping

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[5] Direct carbon dioxide intensity of cement production.
[6] See http://www.wbcsdcement.org/GNR-2015/world/GNR-Indicator_71DGWce-world-2015.html.
[7] Estimated from the following sources: for bricks, blocks, and pavers, https://www.freedoniagroup.com/Bricks-Blocks-Pavers.html; for ready-mix concrete, https://www.statista.com/statistics/291597/revenue-of-ready-mix-concrete-manufacturing-in-the-us/; and for precast concrete, https://www.grandviewresearch.com/industry-analysis/precast-concrete-market.
[8] Cementing binders and their derivatives like concrete present compressive strength that is superior to their tensile strength. For this reason, it is necessary to include either continuous (e.g., embedded steel rebar) or discontinuous (e.g., discrete fibers) reinforcement in such composites to enhance their tensile load-bearing performance.

over distances greater than about 250 miles, unless carried out over water, is often prohibitive. On the other hand, concrete, also a heavy, low-cost product, is often produced closer to the site of consumption. In particular, ready-mix concrete is typically made locally around the time of use from a mixture of cement, water, aggregates, and chemical additives. After the ingredients are mixed, the material can be transported, poured, or otherwise manipulated for only a few hours before it hardens. By contrast, cementing systems based on mineral carbonation show little if any hardening until all the mixed ingredients make contact with CO_2, thereby offering greater control over the workability window. This is significant as the ease of controlling the rheology of such systems makes them potentially better suited for advanced (e.g., additive) manufacturing of structural components which feature superior strength-to-weight ratio, optimized topology, and complex geometries that could not be fabricated using existing casting or molding-based techniques.

Mineral Carbonation Processes

Mineral carbonation can be readily accomplished by contacting alkaline (mineral) solids, such as Ca- or Mg-rich materials, with CO2 in a fluid state or in solution. Depending on the types of alkaline solids used, these reactions can occur readily, even at ambient temperature and pressure. Carbonation often involves dissolution-precipitation reactions, specifically, dissolution of the elemental species from the reactant solid(s) and the solubilization of CO2 into the liquid phase (e.g., water) followed by the precipitation of carbonate mineral solids from a supersaturated solution. This process can result in the formation of many polymorphs of calcium carbonate (CaCO3), including amorphous calcium carbonate, vaterite, aragonite, and calcite. Calcite is the polymorph most often noted to exist at equilibrium (de Leeuw and Parker, 1998), though it is possible to direct the formation of one or multiple polymorphs (Chang et al., 2017ab) by controlling the reaction conditions. In the presence of magnesium, magnesite (hydrated magnesium) carbonate phases may also form, although the formation of these types of carbonates is typically less preferred than their calcium-bearing variants (Pokrovsky, 1998). The need for alkaline reactants is due to the pH-dependent aqueous partitioning of dissolved carbon, in which carbonate ions (CO32−) are the dominant species at pH > 10.33 at 25°C as disclosed by a Bjerrum diagram (Morse and Mackenzie, 1990). Hence, increasing alkalinity results in increasing oversaturation of the solution with respect to CaCO3, favoring its precipitation. The precipitation of CaCO3 from aqueous carbonate is easier than formation from bicarbonate ions (HCO3−), which requires the deprotonation of the bicarbonate ion prior to the formation of CaCO3. The fact that the reaction generally requires caustic conditions in order to advance rapidly is considered the Achilles' heel of the current paradigm of carbonation.

This approach of producing calcium and magnesium carbonates (particularly calcite, aragonite, and vaterite, which are polymorphs of $CaCO_3$, and magnesite, $MgCO_3$) from slurry-borne precursors is the basic pathway that can be exploited to produce mineral aggregates and binders for concrete. Carbonation can be accomplished using reactants including residue brines (e.g., from water desalination; Dindi et al., 2015), low-rank calcium silicates (Bukowski and Berger, 1979), hydrated lime (i.e., portlandite, $Ca(OH)_2$; Moorehead, 1986), coal combustion residues (e.g., fly ash; Montes-Hernandez et al., 2009), and minerals and rocks such as serpentines and basalt (Oelkers et al., 2008). The abundance of Ca or Mg in the substrate is not a sufficient indicator for carbonation. Rather, the mobility and accessibility of Ca or Mg present (i.e., the reactivity of the solids) and the avoidance of surface passivation are critical factors that determine whether a given substrate may be suitable for carbonation processing or not (see Wei et al., 2018), which determines the degree of carbonation ultimately achieved.

The introduction of carbon dioxide into the "cementing formulation" can be plausibly accomplished by the following two pathways: (1) injecting carbon dioxide into the fresh concrete over a short period or (2) exposing preformed components of structural components to vapor-phase carbon dioxide, in dilute or concentrated form on the order of hours, within reactors. Expectedly, these pathways result in different levels of carbon dioxide uptake. For example, carbon dioxide injection into fresh concrete results in uptake that is limited by the overall rate of carbon dioxide reaction with calcium and magnesium, which in turn may be limited by the solubility of carbon dioxide in alkaline aqueous solution (i.e., ≤ 0.01 g CO2 per gram of cementitious components). On the other hand, the exposure of preformed components results in carbon dioxide uptake that is limited by the nature of the reactant used and potentially the geometry of the body, which may result in carbon dioxide transport limitations such that the carbon dioxide uptake typically ranges between 0.05 and 0.50 g CO2 per gram of cementitious components.

The following sections briefly describe a variety of approaches and possible inputs to mineral carbonation.

Residue Brines

Desalination operations, which provide potable water from seawater, and other operations such as oil and gas production generate large quantities of brines that are enriched in magnesium and calcium. When CO_2 in a vapor state is injected into such brines at ambient temperature and pressure, hydrated carbonate products form spontaneously, as long as sufficient pH buffering is provided. While this approach can result in the formation of a wide range of hydrous calcium and magnesium carbonates, kinetic controls on precipitation reactions appear to often favor the formation of nesquehonite $(Mg(HCO_3)(OH) \cdot 2H_2O)$ at the expense of other reaction products (Mignardi et al., 2011).

This approach has been used, for example, to produce nesquehonite-based products that yield comparatively low compressive strengths, on the order of 8 MPa (Glasser et al., 2016).

Low-Rank Calcium Silicates

Low-rank calcium silicates ($CaO/SiO_2 < 2$, molar ratio) are well known to carbonate, especially in the presence of water and elevated CO_2 concentrations. This reaction, often carried out under near-autoclave conditions, can be used to carbonate a range of otherwise slightly hydraulic low-calcium silicates including rankinite (Ca_3SiO_7) and wollastonite (Ca_3SiO_5). The carbonation of low-rank silicates in such a manner yields intermixed calcium carbonate and amorphous silica, which serve as effective binding agents (Bukowski and Berger, 1979). However, to realize favorable reaction kinetics, carbonation reactions in these systems need to be carried out using concentrated CO_2; otherwise, the kinetics are typically too slow for practical exploitation.

Ordinary Portland Cement (OPC)

While low-rank silicates can be carbonated, the constituents of anhydrous OPC ($CaO/SiO_2 \geq 2$, molar ratio) are much more resistant to carbonation. This is because, in the presence of water, there exists a competition between hydration and carbonation, with hydration being the preferred pathway (Young et al., 1974). Even so, under ambient conditions, the reaction products of OPC hydration, for example, $Ca(OH)_2$ and nonstoichiometric C_x-S-H_y phases (calcium-silicate hydrate, often, C = CaO, S = SiO_2, H = H_2O, x = 1.7, and y = 4.0), carbonate, albeit slowly, in the presence of atmospheric CO_2 (0.4% CO_2). However, due to the fine porosity and water saturation prevalent in hydrated OPC, carbonation of hydrated OPC and traditional concrete proceeds very slowly under ambient conditions due to the hindered diffusion of CO_2 (Kashef-Haghighi and Ghoshal, 2013). As a result, it can take years for just the first few centimeters of a concrete to carbonate. Despite this slow rate, the tremendous volume of concrete emplaced worldwide can serve, over time, as a considerable sink for CO_2 (Brady et al., 1996; Galan et al., 2010; Possan et al., 2017). In addition, crushed cementitious construction and demolition wastes in the form of fine particulates could achieve substantial, although inadvertent, CO_2 uptake.

Portlandite

The carbonation of hydrated lime (portlandite, $Ca(OH)_2$, often called slaked lime) has been practiced over millennia (Carran et al., 2012). Hydrated lime mortars take up atmospheric CO_2 at ambient conditions over long periods of exposure, resulting in the formation of calcium carbonate. This process, while far too slow to be practical as a route for CO_2 utilization (similar to the carbonation of hydrated OPC and traditional concrete under ambient conditions), can be greatly accelerated under suitable conditions of temperature, pressure, CO_2 concentration, and relative humidity (which dictates the water saturation state in the pore structure of solids prior to and during carbonation reactions). Similar to atmospheric carbonation, accelerated carbonation of portlandite also results in the formation of a monophasic $CaCO_3$ product (often calcite) with robust cementation properties. The substantial tendency of portlandite to carbonate allows for accelerated carbonation to be accomplished even using relatively dilute streams of CO_2 ($\geq 5\%$ CO_2)—for example, using flue gas emitted by coal, natural gas, or cement plants—as long as suitable conditions of relative humidity and temperature can be maintained. Furthermore, portlandite offers among the highest CO_2 uptake per unit mass (0.59 g CO_2 per gram of portlandite), and its fast reaction kinetics allow near complete carbonation to be achieved over the course of hours (Vance et al., 2015).

Industrial Wastes

Industrial (alkaline) wastes such as fly ash, slags, mine tailings, cement kiln dust, and air pollution control residues constitute the byproducts of coal combustion, metal processing and mining, OPC production, and waste incineration, respectively. Such residues span a diversity of compositions as a function of the (1) parent coal composition, (2) ore-refining process, (3) ore composition, (4) waste make-up, and/or (5) combustion processes. However, in common, each of these industrial wastes features intrinsic alkalinity (e.g., they are mixtures of Ca and Mg with Al, Si, and alkalis) that can be neutralized by reaction with CO_2. As an example, fly ashes can be broadly characterized as being Ca rich (Class C) or Ca poor (Class F) following standardized classifications.[9] While Class C fly ashes are derived from the combustion of lignite or subbituminous coals, Class F fly ashes are derived from the combustion of bituminous or anthracitic coal. Recently, Wei et al. demonstrated an approach for fly ash carbonation wherein slurries of Ca-rich fly ash and water following exposure to dilute, vapor-phase CO_2 offer robust cementation by the in situ formation of calcite (Wei et al., 2018). The carbonation of Ca-rich fly ashes is rapid, and the strength achieved is sufficient for structural construction. The extent of carbonation

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[9] ASTM C618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. ASTM International.

in such systems is critically linked to their mobile (readily reactive) Ca content. As a result, Ca-poor fly ashes offer little if any carbonation and strength gain compared to their Ca-rich counterparts. In fly ashes and other alkaline wastes the Ca and Mg present is not all mobile; as a result, such wastes often display carbonation extents that are substantially inferior to those inferred from their simple oxide (CaO or MgO) compositions (Monkman and Shao, 2006).

Uptake Potential for Mineral Carbonation

Assuming a need for an alternative to OPC at today's production levels, the amount of carbon dioxide that can be utilized—by mineralization—can be established by considering the ability of diverse alkaline solids (e.g., fly ash, blast furnace slag, portlandite, and low-rank silicates) to react with carbon dioxide, thereby producing alkaline carbonates. A range of carbon dioxide uptake can be established by considering fly ashes and portlandite. Fly ashes feature a terminal carbon dioxide uptake of ≤ 0.05 g CO_2 per gram of fly ash, and portlandite features a CO_2 terminal uptake of 0.54 g CO_2 per gram of portlandite over time scales of tens of hours. These uptakes suggest global carbon dioxide utilization levels ranging between 0.2 billion tons for fly ash[10] and 2.2 billion tons[11] for portlandite, if sufficient quantities of these materials were available. Since carbon dioxide mineralization resulting in cementation is expected to be achieved using a diversity of alkaline precursors, with a range of carbon dioxide uptake capacities, a rough estimate of approximately 1 billion tons of carbon dioxide on an annual basis is reasonable.

Carbonation of Ca- and Mg-Bearing Rocks

The formation of natural carbonate-bearing sedimentary rocks occurs through geological processes involving the weathering of rocks on the Earth's surface by their reaction with water, releasing divalent ions such as Ca and Mg, which subsequently combine with CO_2 to form carbonate minerals either through biogenic or abiogenic mechanisms. In certain localities rich in ultramafic and mafic rocks, such as ophiolitic formations, hyperalkaline Ca-rich groundwaters take up CO_2 upon reaching the surface (for example, in springs), rapidly precipitating calcium carbonate in the form of travertine deposits (Kelemen and Matter, 2008). These processes can be mimicked in an accelerated manner by using rocks that are rich in Ca and Mg (e.g., basalt, gabbro, peridotite, and serpentinite) as carbonation reactants. However, because of their much lower reactivity than industrially produced materials, natural crystalline rocks require an initial

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[10] 0.05 g CO_2 /g fly ash $\times$ 4.1 billion tons = 0.2 billion tons of fly ash.
[11] 0.54 g CO_2 /g portlandite $\times$ 4.1 billion tons = 2.2 billion tons of portlandite.

pretreatment process before carbonation. These processes, which can be mechanical (e.g., ultrafine grinding) or thermal (e.g., exposure to temperatures above 600°C to remove chemically bound water), require large amounts of energy (Penner et al., 2004).

Factors Affecting Carbonation Dynamics

A number of factors affect carbonation dynamics and CO_2 uptake of these mineral carbonation approaches. First, carbonation reactions, while often unaffected by flue gas contaminants such as particulate matter and acid gases (e.g., SO_x and NO_x), are sensitive to the presence and state (liquid or vapor) of moisture, which may be present or liberated over the course of carbonation. This is because water, although appropriate for accelerating carbonation reactions on mineral surfaces, when condensed within pores retards the diffusive transport of CO_2 (and hence carbonation kinetics) toward the reactants. Therefore, it is important to control liquid water saturation levels within microstructures, such as when carbonation is carried out in precast components. Second, the solubility of CO_2 decreases with increasing temperature, reducing the concentration of CO_2 in the liquid and promoting precipitation of calcite by decreasing its solubility. Hence, the temperatures over which carbonation reactions are carried out need to be considered and controlled. Third, as is typical for fluid-solid reactions, the surface area of the reactants (particle size) affects reaction kinetics. Although fine particles can accelerate kinetics, their production is energy intensive due to the need for grinding. In addition, their use may complicate slurry processing, due to their tendency to agglomerate, and result in refined microstructures that show retarded liquid and vapor transport.

All of the approaches described above result in the formation of calcium carbonate polymorphs (aragonite, vaterite, calcite; Chang et al., 2017ab) and in certain cases hydrous silica (Ashraf and Olek, 2016), or hydrated calcium silicates, as the reaction products that glue the composite together, thereby imparting strength (Fernández Bertoz et al., 2004). These products are stable under ambient conditions of temperature, pressure, and CO_2 concentration over geological time scales, as evidenced by the widespread deposits of limestone in nature.

Market Considerations

Construction materials including OPC, concrete, and mineral aggregates constitute the largest material flows in the world, second only to water. Each year, nearly 30 billion tons of concrete (World Business Council, 2009) are generated globally from a production base of 4.1 billion tons of OPC (USGS, 2017) and nearly 52 billion tons of mineral

aggregates[12] (which, beyond their use in concrete, find use in engineered barriers and road base applications; Tepordei, 1999). Given the scale of these markets, mineral carbonation products may have the potential to utilize up to 1 gigaton (Gt) of CO_2 annually (Global CO_2 Initiative, 2016) if they were to replace existing products. The large production volumes offer substantial economies of scale for conventionally produced products, resulting in costs on the order of $50 per ton for concrete (Villere, 2015), $100 per ton for OPC, and $10 per ton for aggregates (USGS, 2018). Taken together, these numbers define a cost basis for both existing and emerging construction materials. They also highlight some of the challenges that any new product might face: competition with well-entrenched products with low costs that can be produced worldwide.

In general, concrete, OPC, and aggregates incorporate elements (e.g., Si, O, Al, and Fe) that are abundant in the Earth's crust (≥ 3 mass percent), with minor distributions of Ca, the alkalis K and Na, and Mg (Fleischer, 1953). This abundance ensures that the raw materials required for production, such as limestone and clays, are (1) well dispersed geographically, (2) economical to extract, and (3) available in quantities large enough to satisfy prevailing and anticipated demand over long time scales. There is, for example, sufficient limestone in the Earth's crust to support construction demands for more than 100,000 years (Biernacki et al., 2017). In addition, demolition wastes are also present in large volumes; while construction and demolition wastes may be recycled for use as road base and for limited use as concrete aggregates, the vast majority of these wastes continue to be landfilled (EPA, 2016).

While the construction sector offers large material flows cumulatively, the manufacture of construction materials is a localized activity. For example, there are 5,500 ready-mix concrete plants,[13] hundreds of precast concrete plants,[14] and nearly 100 OPC production plants (Portland Cement Association, 2013) in the United States alone. This localization and fragmentation implies that if mineral carbonation is to be used to produce construction materials that can replace existing materials, (1) CO_2 will need to be consumed in many discrete locations to produce a range of materials and products, and (2) the logistics of CO_2 access and transportation of manufactured products will be critical for economic viability.

There are substantial efforts under way to produce construction materials via mineral carbonation. Most are being undertaken by startup companies and precommercial entities, which fall into two groupings: (1) those producing binding agents in concrete (examples include Solidia Technologies, Carbon Upcycling UCLA, CarbonCure, and

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[12] See https://www.prnewswire.com/news-releases/the-freedonia-group-world-construction-aggregates-to-reach-517-billion-metric-tons-300241261.html.
[13] See https://www.nrmca.org/concrete/data.asp.
[14] Estimated from the number of certified precast plants by National Precast Concrete Association: https://precast.org/certification/, Precast/Prestressed Concrete Institute: https://www.pci.org, etc.

Carbstone Innovation) and (2) those producing synthetic aggregates (examples include Carbon8 Systems and Blue Planet):

- *Solidia Technologies*[15] is using low-rank silicate(s) as the reactant for carbonate mineralization. While low-rank silicates, which feature a CO_2 uptake of up to 0.38 g CO_2 per gram of reactant, can be produced in existing OPC production kilns, their carbonation processing so far involves purified CO_2, secured from industrial suppliers, at superambient conditions. This renders the approach well suited for ex situ production, similar to precast concrete. The reaction products, which include intermixed $CaCO_3$ and SiO_2 (hydrous silica), offer robust cementing behavior.

- *Carbon Upcycling UCLA*[16] is using portlandite and industrial wastes as the primary reactants for carbonate mineralization. The $CaCO_3$ formed in situ serves as the cementation agent. While portlandite, which features CO_2 uptake on the order of 0.59 g CO_2 per gram of portlandite, can be produced in existing OPC production kilns, its carbonation processing, while compatible with dilute CO_2 waste streams (>5% CO_2 v/v), requires the use of slightly above-ambient reaction temperatures. Therefore, the approach is suited for co-located ex situ production, for example, alongside a fossil-fuel power plant or an OPC production plant, which serve as a source of solid reactants, waste CO_2, and/or heat.

- *CarbonCure*[17] injects pure CO_2 into ready-mix concrete formed during initial mixing. The injected CO_2 reacts with either unreacted Ca, liberated from the dissolution of OPC or from OPC replacement materials such as slag or fly ash. The reaction products are formed in situ, then blended with the binder, thereby forming carbonate compounds that contribute to increased and somewhat accelerated strength gain as compared with traditional concrete. The CO_2 uptake is approximately ≤ 0.01 g CO_2 per gram of reactants, following Henry's law. The approach enables reduction in cement use, thus offering the benefit of CO_2 avoidance by reducing the need for traditional OPC production. This approach is currently being implemented across numerous ready-mix concrete plants in the United States.

- *Carbstone Innovation*[18] is using slags produced from iron and steel manufacturing as the alkaline substrate for mineral carbonation. The process involves contacting fine slag particulates in an aqueous suspension with enriched CO_2 resulting in the formation of $CaCO_3$ as the cementing agent. While the CO_2 uptake of slags varies as a function of their composition, it is anticipated that CO_2 uptake on the order of 0.10 g CO_2 per gram of slag can be realized. The approach is best suited for ex situ

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[15] See http://solidiatech.com.
[16] See http://www.co2upcycling.com/.
[17] See https://www.carboncure.com.
[18] See https://www.carbstoneinnovation.be/en/.

production alongside a source of both slags and waste CO_2. It has been used to produce a diversity of preformed products.

- *Carbon8 Systems*[19] is using heterogeneous air pollution control (APC) residues as the alkaline reagent for the production of carbonate aggregates. The process involves contacting APC residues with pure CO_2 supplied by industrial vendors within a formulation containing other binders and fillers where the formation of $CaCO_3$ allows for the creation of carbonate cemented aggregates. The approach yields CO_2 uptake around 0.12 g CO_2 per gram of solid reactants and is well suited for jurisdictions with high landfill use costs. The approach has achieved commercial operations in United Kingdom based on its ability to encapsulate and isolate APC residues in a carbonate matrix.
- *Blue Planet*[20] is using alkaline rock and industrial wastes as the primary reactants for carbonate mineralization. The process involves the formation of synthetic layers of $CaCO_3$ over a substrate, resulting in the formation of synthetic carbonate aggregates in a manner analogous to their formation in nature. The process is thought to be compatible with the use of dilute CO_2 waste streams and is therefore well suited for co-location alongside fossil-fuel power plants or OPC production plants that could serve as a source of solid reactants and/or waste CO_2.

Each of these approaches exploits the thermodynamic ease of mineral carbonation and the potential for cementation offered by calcium carbonate. While these efforts are in the early stage, they highlight the potential for CO_2 utilization in the construction materials markets. However, the scalability and market viability of these approaches are affected by a diversity of factors, including (1) the purity and the availability of CO_2, (2) the availability of low-cost alkaline reagents and/or facilities for their manufacture at scale, (3) the low-cost, commoditized nature of the existing analogous products, OPC and concrete, (4) restrictive building codes and standards wherein compliance is often a function of the material composition (e.g., OPC-based chemistries) rather than their engineering performance, and (5) the net amount of CO_2 utilization that can be achieved.

Net Greenhouse Gas Emissions

Ultimately, a goal of mineral carbonation is to utilize CO_2 in waste gas that would otherwise be emitted into the atmosphere. As a result, it is critical to consider whether mineral carbonation processes produce a net reduction in CO_2 emissions once all the relevant material and energy balances are considered. Mineral carbonation approaches need to be carefully evaluated using consistent methods for life-cycle assessments (see

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[19] See http://c8s.co.uk/.
[20] See http://www.blueplanet-ltd.com.

Chapter 8) to allow clear estimation of *net* CO_2 utilization that is achieved. Such analyses are important to evaluate pathways that may yield the largest levels of CO_2 utilization, thus reducing the accumulation of CO_2 in the atmosphere.

A RESEARCH AGENDA FOR MINERAL CARBONATION

The expanded use of mineral carbonation depends on addressing technical, economic, and market-acceptance criteria. If carbonated materials are to contribute to CO_2 management, each of these factors must be addressed. For example, a technical solution that does not fulfill acceptance criteria or that cannot achieve the tremendous scale required to fulfill construction demands is unlikely to significantly impact industrial practices. Similarly, a product will not succeed if it does not fulfill the relevant engineering requirements. An additional challenge is the physical handling of carbon dioxide. The following sections outline key barriers to commercialization of mineral carbonation technologies along with key areas in which further research could help to overcome those barriers.

Barriers to Commercialization

The development of commercially viable carbonation technologies is impacted by gaps in our understanding of carbonation processes, technical challenges facing various carbonation approaches, and a variety of economic and social factors affecting the potential costs and market penetration of mineral carbonation technologies.

Chemical and Physical Barriers to Carbonation

While carbonation reactions often proceed readily under certain conditions, this is often due to favorable thermodynamics rather than design. Table 3-1 summarizes key barriers to mineral carbonation approaches using various precursors. Carbonation is commonly impeded by one of three factors: (1) competitive reactions, (2) the formation of surface-passivating films, and (3) the presence of water. The first factor is often a function of the tendency of solids to hydrate versus carbonate. As a result, Ca-rich solids that are highly hydratable (e.g., MIII-Ca_3SiO_5, alite; Taylor, 1997) typically show poor potential to carbonate vis-à-vis fully hydrated Ca-rich solids (e.g., $Ca(OH)_2$). The second factor, passivating films, refers to dense films of calcite that form on carbonating surfaces and hinder further contact between the reactant solid and CO_2. The formation of such physical barriers is a key reason why solids such as CaO (lime, a highly hydratable solid) carbonate

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only fractionally (often 10 percent or less at nonisothermal conditions; Montes-Hernandez et al., 2012), following which the reaction is arrested (Nikulshina et al., 2007). The third factor relates to the fact that water favors carbonation when adsorbed on surfaces (Beruto and Botter, 2000) but inhibits carbonation when condensed within the pores of a micro- or mesoporous solid (Burkan Isgor and Razaqpur, 2004; Goracci et al., 2017). This is especially relevant to the case of precast sections that are contacted with CO_2 vapors. Since they are produced from slurries or are dry cast in dense suspensions, wherein mixtures of the solids are intermixed with water for lubricity, such sections feature substantial amounts of water trapped within their pores. Water trapping hinders the transport of vapor-phase CO_2 into the microstructure, even when CO_2 may be solubilized into the pore liquid. This effect becomes more prominent with the size of the sections such that larger components may take longer to carbonate than smaller components following a typical $t^{1/2}$ ("diffusive") scaling for CO_2 penetration (Bouquet et al., 2009).

Barriers to Carbonation Processing

Two major issues that complicate carbonation processing are (1) the need for alkaline precursors that are progressively neutralized following contact with CO_2 and (2) the need for sustained elevated pH levels in solution to promote carbonate precipitation. These requirements are problematic because, first, the production of the alkaline precursors and reactants typically requires high-temperature activation. For example, the production of portlandite ($Ca(OH)_2$) requires the thermal desorption of CO_2 from limestone (i.e., at T ≈ 800°C, p = 1 bar) to produce lime (CaO), which is subsequently hydrated to form portlandite.[21] The portlandite thus formed, following contact with CO_2, carbonates to re-form calcite. Considering that the mineralized CO_2 released from the initially decarbonated limestone can be recaptured (but is not currently), this high-temperature process is, at best, CO_2 neutral when viewed from the perspective of the mineralized CO_2. While this is indeed less CO_2 intensive than the traditional pathway of OPC production, the development of truly CO_2-neutral or -negative pathways requires the development of new scalable low-temperature or hydrothermal routes for producing alkaline precursors, such as from waste streams containing Ca and Mg. Second, because the solubility of $CaCO_3$ diminishes with increasing pH and CO_2's dissolution in water induces acidity (by the formation of carbonic acid, in equilibrium with dissolved CO_2, pKa = 6.35), there is a need for alkaline buffering to sustain the precipitation of carbonates. Therefore, increasing the pH is the key means of accelerating carbonation rates. Therefore, it is necessary to develop chemical additives that can enhance carbonation rates by affecting reaction controls, whether kinetic or thermodynamic. This includes enhancing growth rates (for example, by epitaxial matching; Gehrke et al., 2005), facilitating surface dehydration to ease ion attachment or other

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[21] See https://www3.epa.gov/ttnchie1/ap42/ch11/final/c11s17.pdf (accessed October 10, 2018).

interactions with adsorbed water (Ricci et al., 2017), and surface complexation that promotes subsequent adsorption and heterogeneous growth (Brady et al., 1996). These approaches could improve carbonation rates while reducing the extent of basicity that is needed to sustain fast mineral carbonation kinetics.

Availability and Suitability of CO_2 Streams

While the pressure, temperature, and CO_2 concentration required to achieve optimal reaction conditions for mineral carbonation remain largely unknown, it is clear that, for most alkaline reactants, kinetics is favored by increasing CO_2 concentration (Cui et al., 2015; Sun et al., 2008). There exist significant industrial sources of concentrated CO_2 streams which may present opportunities for carbon dioxide utilization (see Chapter 2). However, the vast majority of waste CO_2 streams are dilute ($\leq 25\%$ CO_2 v/v). Thus, for most alkaline feedstocks there is a need for either low-cost CO_2 capture systems or the ability to handle large volumes of gas streams containing components other than CO_2. A further complication is that dilute CO_2 is most often available distant from major construction markets (cities). This may necessitate (1) the co-location of manufacturing facilities for carbonated materials alongside CO_2 emissions sites, which may also offer waste heat that favors the advancement of chemical reactions, or (2) transporting CO_2 to production and consumption centers. These aspects may impose additional costs related to CO_2 capture and/or transport, especially since current CO_2 distribution pipeline networks are limited; in the United States, for example, these exist primarily in Texas and Oklahoma (DOE, 2015) (see Figure 7-3). Broadly, in light of the low profit margins of the commoditized construction materials sector, it appears prerequisite to maximize the use of dilute CO_2 streams. While concentrated and purified CO_2 is supplied by vendors for a fee, dilute, unprocessed CO_2 could conceivably be sourced at little or no cost, or at presumably the equivalent of a landfill tipping fee, so long as it could be consumed in proximity to its site of production.

Costs and Abundance of Precursors and Mineral Carbonation Products

OPC and coal combustion wastes are produced at industrial scales worldwide. As such, global production of these materials is currently on the order of 4.1 billion and 1 billion tons on an annual basis for OPC and coal combustion wastes, respectively, with pricing on the order of $100 per ton, and $10 to $100 per ton (depending on location and the material's suitability for use in traditional concrete[22]), respectively. Reactants

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[22] For example, compare the prices of crystalline versus ground granulated blast furnace slag (U.S. Geological Survey Mineral Commodities Summary,

appropriate for carbonation, including portlandite and wollastonite ($CaSiO_3$, a low-rank silicate), are currently produced at a global level approaching 350 million tons (USGS, 2017) and 0.8 million tons, respectively.[23] In principle, OPC, hydrated lime, and wollastonite can all be produced using similar facilities (such as typical OPC plants), as long as suitable raw materials are available in the local vicinity. As such, based on volume scaling and the availability of raw materials, it might be possible to produce portlandite and wollastonite at cost parity to OPC, and with considerably reduced CO_2 intensity due to the reduced synthesis temperatures needed (Zulumyan et al., 2015) and their lower molar content of CaO per unit mass. While coal combustion wastes are currently readily available, this may change with a transition away from coal-fired electricity generation. It is unlikely that production of carbonated aggregates will be produced at cost parity compared to quarrying. Therefore, absent suitable incentives, carbonated binders may offer a more market-viable proposition than carbonated aggregates.

Shipping of construction materials, whether as constituents or as preformed elements, is expensive on account of their substantial bulk. Thus, their transport is cost effective only over a few hundred miles, if by road. While rail or over-water transport may be more cost effective in some cases, it typically requires shipment of much larger quantities of product. These logistical limitations suggest carbonation technologies may be most effectively implemented at multiple discrete sites rather than at large centralized operations, reducing the economies of scale.

Construction Codes and Standards

In general, it is desirable that a new product achieves performance equivalence, or ideally performance benefits, vis-à-vis a product that it is intended to displace. While this argument is logical for the vast majority of applications in construction, its application in the context of OPC-based products may differ. This is because the construction sector has gained empirical confidence in the use of OPC and traditional concrete as construction materials, and construction industry standards are notoriously slow to change (see Chapter 9). Furthermore, construction standards and codes are often jurisdictional (e.g., city by city or state by state). This results in fragmented compliance and acceptance standards that may inhibit or delay the market entry and adoption of new products. A further complication is that construction standards are often prescriptive rather than performance based; as such, they often define the compositions of materials that can be used. Pending external forcing through legislation (e.g., see AB262: Buy Clean California Act[24] and AB32: Global

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https://minerals.usgs.gov/minerals/pubs/commodity/iron_&_steel_slag/mcs-2018-fesla.pdf) and of compliant versus noncompliant fly ash (Concrete Construction – Fly Ash).
http://www.concreteconstruction.net/_view-object?id=00000153-8b9c-dbf3-a177-9fbd58630000).
[23] See https://minerals.usgs.gov/minerals/pubs/commodity/wollastonite/mcs-2017-wolla.pdf.
[24] See https://leginfo.legislature.ca.gov/faces/billNavClient.xhtml?bill_id=201720180AB262.

Warming Solutions Act[25]), preferential government purchasing programs, or the imposition of CO_2 taxes and penalties, this is a substantial challenge that has to be overcome before the use of carbonated materials can become widespread within the construction sector. Among other elements, this requires moving to a system of harmonized performance-based standards, which will accelerate the adoption and acceptance of new materials for construction applications and new tools that can model and predict long-term performance of new materials.

TABLE 3-1 Summary of key chemical and physical barriers associated with selected mineral carbonation inputs.

Input	Key Barriers
Mature OPC-based concrete	At ambient conditions under mass transfer (diffusion) control, it takes years for carbonation to occur.
Fresh OPC-based concrete	Reaction rates are slow at ambient conditions. Carbon dioxide concentration in the slurry is limited. Moreover, carbonation is impeded in the presence of moisture.
Low-rank calcium silicates	A high concentration of CO_2 is needed to achieve sufficiently fast reaction kinetics.
Hydrated lime	In dilute CO_2, favorable reaction conditions require the maintenance of slightly above-ambient temperature conditions.
Industrials wastes (e.g. fly ash, slags, etc.)	The heterogeneity of these wastes results in broad variations in reaction kinetics, with their CO_2 uptake being substantially lower than that estimated from their bulk oxide composition.

Priority Research Areas

Mineral carbonation offers great potential for CO_2 utilization in the short to medium term. While the technology for mineralization processes is farther along than for many chemical and biological conversion pathways, further research and development is needed to address key barriers in mineral carbonation technologies, processing, and market adoption. Priority research areas include controlling carbonation reactions, process design,

[25] See https://www.arb.ca.gov/cc/ab32/ab32.htm.

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accelerating carbonation and crystal growth, green synthesis routes for alkaline reactants, structure-property relationships, analytical and characterization tools, and construction methodologies.

Controlling Carbonation Reactions

Research is needed to understand the fundamental chemical features that control the relative rates of carbonation and hydration. This will lead to improved selection of alkaline solids and reaction conditions.

Process Design

Research is needed to integrate mineralization processes with existing carbon dioxide capture technologies. This will lead to increased process performance and ensure optimal carbon dioxide conversion rates and energy use efficiencies.

Accelerating Carbonation and Crystal Growth

Research is needed to develop additives for enhanced carbon dioxide solubility or structure-directing agents that accelerate particle growth. This will accelerate carbonation reactions such as crystal growth rates in solution beyond what is achieved simply by increasing the pH.

Green Synthesis Routes for Alkaline Reactants

Research is needed to develop energy- and carbon dioxide–efficient pathways and processes for producing alkaline solids that can be readily carbonated and do not require high-temperature activation. This will lead to energy and carbon dioxide efficient pathways

Structure-Property Relationships

Research is needed to develop physical and instrumental assessment methods, improved modeling, and performance-based criteria for product properties. This will improve predictions of structure-property relations and increase the durability, viability, and acceptance of carbonated solids.

Analytical and Characterization Tools

Research is needed to develop new analytical tools for studying carbonation reactions in dense and viscous suspensions, as well as the evolution of microstructure across length scales. This will lead to new scientific tools to characterize mineralization technologies.

Construction Methodologies

Research is needed to develop new material formulations with novel properties and to advance the use of additive manufacturing to construct components with superior strength-to-weight ratio, optimized topology, and more complex geometries compared to what can be made with existing construction methods. This will enable new categories of carbon utilization products.

FINDINGS AND RECOMMENDATIONS

Finding 3-1 CO_2 utilization through the production of carbonate-based construction materials (binding agents, mineral aggregates, and concrete) appears to be closest to application at commercial scale compared to other emerging CO_2 utilization technologies.

Finding 3-2 The engineering properties, performance, and long-term chemical durability of mineral carbonation–based construction materials need to be better established for such materials to gain acceptance as substitutes for today's base materials.

Finding 3-3 The purity, pressure, and temperature of CO_2 sources affect the suitability of a given CO_2 waste stream for a given mineral carbonation pathway. However, such criteria remain undefined for the vast majority of mineral carbonation technologies.

Finding 3-4 Mineral carbonation and carbonate formation may be accomplished by a multiplicity of pathways. To better understand such pathways at the molecular level it is necessary to develop improved tools for in situ analysis, characterization, and computational modeling to describe the rheology of concentrated suspensions, the reaction kinetics of carbonation processes, and the evolution of microstructures during reaction and/or phase transformations.

Finding 3-5 Given the very large material flows in the construction sector, this industry offers a tremendous potential for CO_2 utilization. However, matching and integrating CO_2 from widely distributed sources with a diversity of potential consumers and construction product types and markets poses logistical and commercial challenges.

Finding 3-6 The production of construction materials via mineral carbonation has the potential to consume ~1 Gt of CO_2 annually. However, to do so, such construction materials must be able to displace existing products that are currently produced globally at low cost and in large volumes.

Recommendation 3-1 Researchers should continue research efforts to control carbonation reactions by understanding the fundamental chemical features that govern relative rates of carbonation and hydration.

Recommendation 3-2 Researchers should integrate mineralization process with existing carbon dioxide capture technologies.

Recommendation 3-3 Researchers should continue to develop additives for enhanced carbon dioxide solubility or structure directing agents which will help accelerate carbonation and crystal growth.

Recommendation 3-4 Researchers should focus on energy- and carbon dioxide–efficient pathways and processes for producing alkaline solids that can be readily carbonated and do not require high-temperature activation.

Recommendation 3-5 Researchers should increase efforts in developing physical and instrumentation assessment methods, improved modeling, and performance-based criteria for product properties to improve predictions of structure-property relations which will increase durability, viability, and acceptance of carbonated solids.

Recommendation 3-6 Researchers should increase attention to developing new analytical tools for studying carbonation reactions in dense and viscous suspensions, as well as the evolution of microstructure across length scales.

Recommendation 3-7 Researchers should continue research efforts to develop new material formulations with novel properties and to advance the use of additive manufacturing to construct components with superior strength-to-weight ratio, optimized topology, and more complex geometries.

Recommendation 3-8 Critical chemical, physical, and market-acceptance data should be acquired, analyzed, and disseminated by researchers to enable the widespread use of mineral carbonation–based binding agents and aggregates at scale and over broad geographic areas.

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4

Chemical Conversion of CO₂ into Chemicals and Fuels
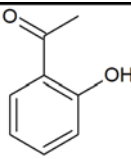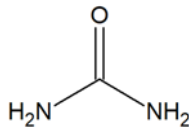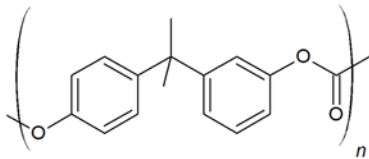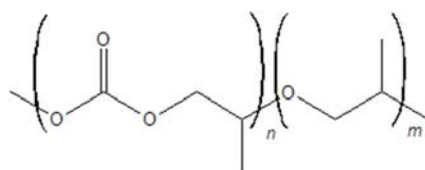
INTRODUCTION

Scientists have been aware of the potential economic and environmental benefits of using CO_2 as a feedstock for the synthesis of commodity chemicals and fuels for decades. It is a generally inexpensive waste product, which contributes significantly to global warming. Nevertheless, despite the large amount of fundamental research that has been performed regarding the conversion of CO_2 into more valuable products there are relatively few examples of industrially viable processes. The challenges associated with the conversion of CO_2 are primarily related to both its kinetic and thermodynamic stability. CO_2 cannot be converted into commodity chemicals or fuels without significant inputs of energy and contains strong bonds that are not particularly reactive. As a consequence, many of the available transformations of CO_2 require stoichiometric amounts of energy-intensive reagents. This can often generate significant amounts of waste and can result in large greenhouse gas footprints. The grand challenge for converting CO_2 waste streams into useful products is to develop processes that require minimal amounts of nonrenewable energy, are economically competitive, and provide substantial reductions in greenhouse gas emissions compared to existing technology. In this chapter we provide an assessment of the current state of research into chemical pathways for the conversion of CO_2 into commodity chemicals and fuels. Areas of promise are identified and technological limitations are highlighted, focusing on the technical features of the CO_2 conversion step. Issues related to enabling technology are covered in Chapter 7, and economic considerations of conversion processes are covered in Chapter 9. Additionally, niche processes which could only be practiced on a small scale and likely could not be generalized to a larger application, for example, the late-stage carboxylation of organic molecules for pharmaceutical synthesis, are not covered, even though there is considerable research activity in this area.

Currently only a limited number of commercial processes that involve the conversion of CO_2 into value-added chemicals exist (Table 4-1) (Patricio et al., 2017; Quadrelli et al., 2011; Topham et al., 2014). Two notable examples are the synthesis of salicylic acid (89.8 kilotons produced worldwide in 2015), which was developed in the 19th century (Lindsey and Jeskey, 1957) and the synthesis of urea (164 million tons produced worldwide in 2013) which was developed in 1922 (Artz et al., 2018). CO_2 is combined with ammonia for urea synthesis. However, it should be noted that the CO_2 used in urea synthesis typically is produced from methane steam reforming, which also produces

the H_2 required for ammonia synthesis. The use of CO_2 from a waste stream for sustainable urea synthesis would require using water electrolysis to make H_2 or an alternative ammonia synthesis.

TABLE 4-1 Major commodity chemicals that are currently synthesized from CO_2 on an industrial scale globally.

Chemical	Scale per year[a]
Salicylic acid	89.8 kilotons
Urea	171,000 kilotons
Cyclic carbonates such as Ethylene carbonate Propylene carbonate	80,000 tons
Polycarbonate	600 kilotons
Polyether carbonate	10 kilotons

[a] Global amount produced using a process involving CO_2.

In the 1950s, methods for the commercial synthesis of cyclic carbonates from CO_2 were developed (Sakakura et al., 2007). Specifically, treatment of CO_2 with ethylene or propylene oxide in the presence of a basic catalyst generates ethylene carbonate or propylene carbonate, respectively. Similarly, styrene oxide, cyclohexene oxide, and 1,3-propylene oxide can also be used as substrates with CO_2 but the cyclic carbonates that are produced are made on a significantly smaller scale. Overall, approximately 80,000 tons of cyclic carbonates were produced worldwide from CO_2 in 2010 (Alper and Yuksel-Orhan, 2017). CO_2 has also been used as a feedstock for the synthesis of aromatic and aliphatic polycarbonates. The Asahi-Kasei process, which generates 600,000 tons of polycarbonate per year, uses CO_2, ethylene oxide, and bisphenol A as feedstocks (Fukuoka et al., 2007). Ethylene glycol, a commodity chemical, is produced as a stoichiometric by-product. Recently, Covestro developed a plant for the copolymerization of CO_2 with propylene oxide to generate polymeric polyols (polyether carbonates), branded as cardyon® (Langanke et al., 2014). These polyols are used to make polyurethanes, which are found in foam mattresses. The CO_2 is obtained from nearby ammonia production. Approximately 5,000 tons per year of polymeric polyols are produced in this facility. Novomer developed a related process, purchased by Saudi Aramco and branded Converge®, for the generation of polyols from CO_2 and propylene oxide, which is being performed on a scale similar to the Covestro system, using the facilities of Centauri Technologies in Texas. In the case of both the Converge® and cardyon® processes, the scale at which the CO_2-derived polyols are produced is approximately 60 times smaller than conventional polyol plants. Whether this technology will eventually replace existing plants and can be performed on a larger scale remains unclear.

The limited examples described above are established technologies (with the exception of polyether carbonate production, which is still undergoing development related to the scale of the process) that are generating products which are available commercially. They will not be discussed further. Instead in the following sections emerging technologies for the conversion of CO_2 into commodity chemicals and fuels are evaluated. Initially, specific products are discussed, before a section on research challenges that extend across products. At the conclusion of the chapter short- and long-term research needs and opportunities are described.

EMERGING TECHNOLOGIES FOR CO₂ CONVERSION INTO COMMODITY CHEMICALS AND FUELS BASED ON PRODUCT

Methanol Production

Methanol (CH_3OH), produced globally on a scale of approximately 70 million tons in 2015, typically is synthesized from syngas ($H_2 + CO$) obtained directly from fossil fuels

(Álvarez et al., 2017; Ganesh, 2014; Pérez-Fortes et al., 2016b; Saeidi et al., 2014). A small amount of CO_2 (up to 30 percent) is generally added to the feed to improve performance (Jadhav et al., 2014). This is successful in part because the mechanism of methanol production involves the initial conversion of CO and H_2O to CO_2 and H_2 via the water gas-shift reaction (Eq. 1). In fact, the development of methods to increase the amount of CO_2 in the syngas feed without causing a large decrease in methanol yield represents an opportunity to utilize waste CO_2 that is produced during syngas production. Although this strategy is only viable if excess H_2 is available, it could improve current technology and increase plant efficiency.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (Eq\ 1)$$
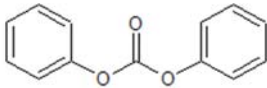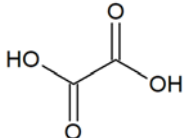
The *direct hydrogenation* of CO_2 to methanol could provide a more sustainable synthetic route if coupled with low-carbon methods for the production of H_2 (refer to Chapter 7) (Álvarez et al., 2017; Ganesh, 2014; Pérez-Fortes et al., 2016b; Saeidi et al., 2014). Furthermore, the development of a practical method for the synthesis of methanol from CO_2 could also facilitate a transition toward a methanol economy, in which methanol is used either directly as a fuel or as a source of H_2 (Olah, 2005).

Researchers have developed several catalysts and reactors for direct hydrogenation of CO_2 to methanol, but high rates and high methanol selectivity have only been possible using high pressures (>300 bar) (Álvarez et al., 2017; Klankermayer et al., 2016; Wang et al., 2015). The cost of this technology presently is not competitive with the cost of methanol synthesis from syngas. Nevertheless, due to special circumstances related to location, presently two large pilot plants for direct methanol production from CO_2 are in operation. The Mitsui Chemical Company in Japan produces around 100 tons of methanol per year from CO_2 (Table 4-2) (Quadrelli et al., 2011). The CO_2 is a waste product generated in an adjacent petrochemical facility, while the H_2 is either also a waste product from the petrochemical industry or generated through the electrolysis of water using photovoltaic devices. The close links to the petrochemical industry make the process economically viable. Second, Carbon Recycling International, located in Iceland, produces approximately 4,000 tons of methanol from CO_2 each year (Klankermayer et al., 2016). The plant uses hydro and geothermal energy to produce H_2 and uses CO_2 captured from the flue gas of a geothermal power plant, which is located next to the CO_2-to-methanol facility. The process is economically feasible because of the availability of low-cost electricity, required to generate the H_2, in Iceland, and because the composition of the flue gas is 85-90 percent CO_2. This substantially lowers the cost of CO_2 compared with more traditional flue gas streams which contain lower amounts of CO_2 (see Chapter 2).

Improved catalysts are critically needed if the direct hydrogenation of CO_2 to methanol is to replace methanol production from syngas. At this stage, significant amounts of research into the direct hydrogenation of CO_2 to methanol have focused on using

heterogeneous copper-based catalysts that are closely related to those used for CO conversion to methanol (Ganesh, 2014). In recent years there have also been a number of reports of catalysts for CO_2 hydrogenation to methanol which use metals other than copper and show promising activity (Martin et al., 2016; Studt et al., 2014). Two general challenges for catalyst development are product inhibition by water (the by-product of CO_2 hydrogenation) and poor selectivity because of the competing reverse water gas-shift reaction between CO_2 and H_2 to generate CO and H_2O. Once more efficient catalysts are developed, further attention can be given to factors such as stability, cost, sustainability, and scale-up potential. Additionally, although ultimately a large-scale catalyst for direct methanol hydrogenation will almost certainly be heterogeneous, research into homogeneous catalysts, which is occurring in the academic community, may prove valuable for guiding the development of heterogeneous systems and for niche applications where a small amount of methanol is generated, for example as fuel to power a portable device (Wang et al., 2015).

TABLE 4-2 Major fine and commodity chemicals that are currently synthesized from CO_2 on a pilot plant scale (a pilot plant is defined as a precommercial system, which produces a chemical or fuel on a smaller scale than a full plant and is used for learning purposes).

Chemical	Company (Location)	Scale per Year[a]
Methanol	• Carbon Recycling International (Iceland) • Mitsui Chemical Company (Japan)	4,000 tons 100 tons
Methane	• Audi (Germany)	1,000 tons
Carbon monoxide (via SOEC)[b]	• Haldor-Topsoe (Denmark)/Gas Innovations (USA)	12 N m³/h
Fuel (via CO_2-based Fischer-Tropsch)	• Sunfire (Germany) • INERATEC (Finland)	3 tons 200 L
 Diphenyl carbonate	• Shell (Singapore) • Asahi-Kasei	500 tons 1,000 tons
 Oxalic Acid	• Liquid Light/Avantium (Netherlands)	2.4 tons

[a] Amount of product that is produced per year. [b] SOEC = solid oxide electrolyzer cell.

Finally, research is currently ongoing into the electrochemical reduction of CO_2 to methanol in which protons and electrons are used as the H_2 source. To date, however, most work reports the formation of methanol as a by-product, at selectivities less than 15 percent (Costentin et al., 2013). Several intermediates formed along the six-electron reduction pathway can release from the catalytic surface to form other products. Recently, it was reported that a molybdenum-bismuth bimetallic chalcogenide electrocatalyst could generate methanol with a Faradaic efficiency (see Glossary in Appendix A) exceeding 70 percent, although this catalyst requires an acetonitrile/ionic liquid electrolyte solution (Sun et al., 2016b). Further exploratory and mechanistic research will be required to identify even more selective (and stable) catalysts that do not require organic electrolytes before electrocatalytic methanol production from CO_2 can be considered for larger-scale application. Alternatively, methanol could be synthesized indirectly, via the initial electroreduction of CO_2 to CO (see below), followed by the conversion of CO to methanol using the processes highlighted above.

Dimethyl Ether Production

Dimethyl ether, which is closely related to methanol (dehydration of methanol gives dimethyl ether), is a platform chemical widely used as an alternative to liquified petroleum gas as a clean fuel (Quadrelli et al., 2011). Currently, dimethyl ether is synthesized either via methanol dehydration or from syngas. For similar reasons to those described for methanol, the direct conversion of CO_2 to dimethyl ether is attractive. The Korea Gas Corporation has developed an indirect strategy for dimethyl ether synthesis from CO_2 that is performed on a scale of 100 tons per day. It involves the tri-reforming of methane, CO_2, and H_2O into syngas (see Chapter 6). The syngas is then converted into dimethyl ether. Although this route is scalable it is not economically viable and does not involve the direct conversion of a CO_2-only feedstock into dimethyl ether. Most likely research into CO_2 hydrogenation to methanol will also provide insight into the formation of dimethyl ether and, if a practical catalyst for direct methanol formation is obtained, a system for dimethyl ether may follow shortly thereafter.

Formic Acid Production

Formic acid is used as a preservative, insecticide, or reducing agent primarily in the food, textile, and pharmaceutical industries (Klankermayer et al., 2016). In 2013, the global production of formic acid was 620 kilotons. The most common method for the synthesis of formic acid is a two-step process involving the initial reaction of CO with methanol to form methyl formate, followed by the conversion of methyl formate to formic acid either through reaction with ammonia to generate formamide and subsequent acidification with

H_2SO_4, or through direct hydrolysis with water (see Scheme 4-1). This direct hydrolysis requires high pressure and a large excess of water, followed by a rapid reduction of the pressure and cooling to generate the formic acid. The conversion of CO_2 to formic acid using either H_2 or protons and electrons represents an atom-economical approach to a valuable commodity chemical, which could potentially become even more important if formic acid is used as a H_2 vector (Pérez-Fortes et al. 2016a; Sordakis et al., 2018).
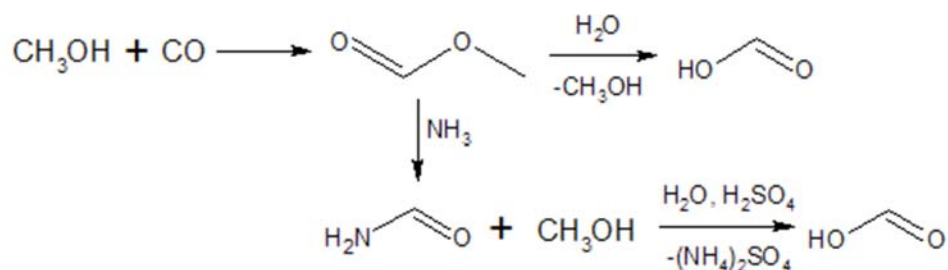
SCHEME 4-1 Industrial synthesis of formic acid.

The thermal hydrogenation of CO_2 to formic acid is thermodynamically unfavorable when starting from gas-phase reactants but becomes slightly exergonic when performed under aqueous conditions (Álvarez et al., 2017; Sordakis et al., 2018). Nevertheless, in academic research, a variety of strategies are typically used to drive the reaction, including using a base to deprotonate the formic acid, generating an ester by reacting formic acid with methanol (or a higher-order alcohol) in situ, or removing formic acid as it is formed. On a laboratory scale, a vast number of homogeneous and heterogeneous catalysts for CO_2 hydrogenation to formic acid have been developed (Álvarez et al., 2017; Sordakis et al., 2018). In some cases these catalysts give high turnover numbers and frequencies but typically only in the presence of a base, which reduces atom economy and increases cost. Challenges for future research into the development of systems for the hydrogenation of CO_2 to formic acid include (i) the discovery of catalyst systems which give high turnover numbers in the absence of base or with recycling of the base, (ii) the need for cheaper ligands to stabilize homogeneous catalysts, and (iii) the refinement of strategies to separate formic acid from the reaction media, which will be a crucial part of successful catalyst commercialization.

Electrochemical and photochemical systems for the conversion of CO_2 and protons and electrons to formic acid have also been developed (Costentin et al., 2013; White et al., 2015). A number of photocatalysts (most typically Si and TiO_2 semiconductor-based materials) have been reported for CO_2 reduction of CO_2 to a variety of C_1 products, including formic acid, but their rates tend to be very low (White et al., 2015). At this point these catalysts and associated photoreactor designs do not show promise for efficient and economic CO_2 reduction at scale. The electrocatalytic reduction of CO_2 to formate has been reported at Faradaic efficiencies (FEs) in the range 80-95 percent using tin-based catalysts (Kumar et al., 2017; Zhang et al., 2014) at moderate to high overpotential, both

in standard three-electrode electrochemical cells and in liquid electrolyte-based electrolysis flow cells, the latter at a rate of 200 mA/cm^2 (Whipple et al., 2010). Palladium nanoparticle electrodes reduce CO_2 to formate with >90 percent FE at <200 mV overpotential, but the palladium requires periodic regeneration because of poisoning by trace CO, which is produced as a by-product (Jiang et al., 2018; Min and Kanan, 2015; Stalder et al., 1984). Palladium has also been used recently as a cathode in a photoelectrochemical device for formate synthesis. The Joint Center for Artificial Photosynthesis has demonstrated 10 percent efficient light-to-formate energy conversion using a Pd/C cathode wired to a tandem III-V GaAs/InGaP photoanode coated with a protective conductive TiO_2 layer (Zhou et al., 2016).

More recently Dioxide Materials reported the reduction of CO_2 to formic acid at a Faradaic efficiency of 94 percent at a rate of 200 mA/cm^2 using a three-compartment electrolyzer with a cation-anion exchange membrane that exhibited stable performance for 500 hours (Yang et al., 2017). Technoeconomic and life-cycle analyses suggest that electroreduction of CO_2 to formic acid has promise and gradually is moving toward scale-up and commercialization (Pérez-Fortes et al., 2016a). Remaining challenges for electrochemical conversion of CO_2 to formic acid include (1) achieving sufficient stability and durability for both catalysts and electrodes and (2) the refinement of energy-efficient strategies to separate formic acid from the product stream (typically a 5-20 wt% aqueous solution).

Methane Production

Methane is widely used as a fuel and to make syngas (3,500 billion cubic meters of natural gas were consumed in 2014) (EIA, 2017). Industrially, it is predominantly obtained directly from natural gas and is rarely synthesized. Nevertheless, the Sabatier reaction, which hydrogenates CO_2 to methane using a nickel catalyst, has been known for more than a hundred years (Eq 2) (Su et al., 2016).

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O \quad \text{(Eq 2)}$$

Small-scale pilot plants based on related heterogeneous catalysts that typically operate at around 300°C were tested in Norway using CO_2 from flue gas and low-carbon H_2, and in Japan and the United States using H_2 from water electrolysis (Quadrelli et al., 2011). This occurred before the widespread production of methane in natural gas from shale resources. Currently, Germany has several small-scale plants, including a pilot plant run by Audi (Table 6-2), developed due to Germany's dependence on renewable energy, which requires systems for energy storage. However, research is also continuing on the design of improved catalysts (Su et al., 2016). Specific challenges that need to be addressed include the development of catalysts that operate at lower temperatures (<200°C) where

the reaction is more favorable and the sintering and oxidation-induced deactivation in nickel-based catalysts can be prevented. Although ruthenium catalysts have shown advantages compared to nickel systems for solving these problems, they have additional cost. At this stage, the hydrogenation of CO_2 to methane is not practical on a large scale and is unlikely to be so in the near future given the low price and abundant availability of methane from natural gas. Additionally, there will be a significantly greater economic value in converting CO_2 to many other chemicals compared with methane.

Electrochemical reduction of CO_2 to methane is also a widely studied process with reported Faradaic efficiencies in the range of 80 to 94 percent using N-doped carbon or copper-on-carbon catalysts in standard three-electrode or H cells (Manthiram et al., 2014; Qiu et al., 2017; Sun et al., 2016a). Partial current densities for methane formation as high as 38 mA/cm^2 have been reported for a Cu catalyst electrodeposited on a carbon gas diffusion electrode (Qiu et al., 2017). As for the aforementioned thermochemical CO_2-to-methane processes, at this time the electrocatalytic conversion of CO_2 to methane, despite continued progress in the development of more selective catalysts, probably will not be pursued on a large scale given the global availability of low-cost methane derived from natural gas.

Carbon Monoxide Production

Carbon monoxide (CO) is an important feedstock in the synthesis of many chemicals and fuels (Keim, 1989). For example, hydrogenation of CO can generate methanol, or through the Fischer-Tropsch process higher-order hydrocarbons can be produced (Eq 3).

$$(2n + 1)\, H_2 + n\, CO \longrightarrow C_nH_{2n+2} + n\, H_2O \quad (Eq\ 3)$$
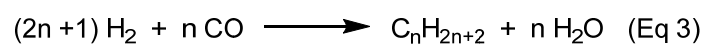
Typically, CO is obtained through the partial oxidation of coal or hydrocarbons at very high temperatures (>800°C). The CO generated from these reactions is not pure, with H_2 being the main contaminant. For many applications a mixture of CO and H_2 is required, but for some applications gas separation is subsequently needed to isolate pure CO.

One method to convert CO_2 to CO is the reverse water gas-shift reaction (Eq 1), in which CO_2 and H_2 are converted into CO and H_2O (Wang et al., 2011). The reverse water gas-shift reaction is an endothermic reaction and consequently high temperatures (~500°C) are typically utilized to favor the formation of CO. Even then a large excess of either CO_2 or H_2 or the constant removal of products are often used as strategies to increase conversion. A range of heterogeneous catalysts have been used for the reverse water gas-shift reaction, including copper- iron-, or ceria-based systems, but in general they have poor thermal stability, and methane is commonly formed as an undesired side product (Wang et al., 2011). Fluidized bed reactors give greater conversion to CO than fixed bed

reactors and this is one approach to improve conversion. Nevertheless, given the thermodynamic limitations of the reverse water gas-shift reaction and the fact that other potential routes to generate CO from CO_2 are at a significantly more advanced state (see below), it is unlikely that research on the reverse water gas-shift reaction for generating large amounts of CO will advance beyond the research stage. However, there may be benefits associated with combining the reverse water gas-shift reaction and Fischer-Tropsch chemistry to generate fuels as described in a subsequent section.

Currently, there are no catalysts (either homogeneous or heterogeneous) for the direct thermochemical reduction of CO_2 to CO and O_2. In contrast, the direct electrochemical splitting of CO_2 to CO and O_2 may provide an alternative to the conventional fossil fuel–based synthetic route (Qiao et al., 2014; White et al., 2015). This reaction can be performed either at high temperature using a solid oxide electrolysis cell (SOEC) or at low temperature using a solution-phase or gas diffusion electrolysis cell. SOECs for CO_2 splitting have recently been brought to market, while low-temperature systems are still in a research phase. Below we summarize the status and remaining challenges for developing both of these technologies.

SOECs are monolithic devices composed of two electrodes separated by a solid oxide-conducting (O^{2-}) electrolyte (Ebbesen et al., 2014; Zhang et al., 2017). A commonly used combination consists of an yttria-stabilized zirconia (YSZ) solid oxide electrolyte, a composite Ni-YSZ cathode, and a perovskite-type anode such as strontium-doped lanthanum manganate. For CO_2 electrolysis, CO_2 is supplied to the cathode side and the anode side is swept with air or another gas. The cathode reduces CO_2 to CO and O^{2-}, which migrates through the oxide-conducting electrolyte to the anode, where it is oxidized to O_2. High temperatures (700-900°C) are required to attain sufficient oxide conductivity in the electrolyte. Under operating conditions, the temperature is maintained by the Joule heating from the internal resistance in the cell itself, which imposes a small energetic penalty but avoids the need to actively heat the system.

SOECs operate at high current densities (0.2 up to 2 A cm^{-2}), achieve high energy efficiency (typically >95 percent), and can produce CO product streams of high purity (>99 percent). Researchers have demonstrated relatively stable performance for CO_2 electrolysis at current densities up to 0.5 A cm^{-2}, with small cell voltage increases observed over several hundred hours of continuous operation (Ebbesen and Mogensen, 2009; Ebbesen et al., 2014). Degradation is faster at higher current densities. Haldor Topsoe[1] currently sells a commercial SOEC system for onsite CO production that provides CO at 99.0 to 99.999 percent purity and requires 6-8 kWh of power per normal cubic meter (Nm^3) CO produced. The first commercial system with 12 Nm^3 h^{-1} capacity began operating at Gas Innovations in Texas in 2016 (Mittal et al., 2017).

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[1]See https://www.topsoe.com/processes/carbon-monoxide/site-carbon-monoxide (accessed October 10, 2018).

There is room for substantial improvement in SOECs to increase deployment of this technology. Major challenges include developing new electrodes with enhanced stability at higher current densities, finding electrolytes that provide high oxide conductivity at lower temperatures, and increasing the tolerance to impurities.

In the past 20 years a large number of molecular and heterogeneous systems for low-temperature CO_2 electroreduction to CO have been developed (Costentin et al., 2013; Ganesh, 2016; Lim et al., 2014; Spurgeon and Kumar, 2018). Faradaic efficiencies in the range 95-98 percent can be achieved routinely in standard three-electrode or H-type cells using a variety of neutral or acidic electrolytes, typically using silver cathode catalysts, resulting in rates of 2-10 mA/cm^2 (Mistry et al., 2017; Neubauer et al., 2016). Interestingly, there are also a number of reports that use non–precious metal catalysts, such as N-doped carbon or carbon nanofibers, achieving performance levels that are similar as those obtained with silver catalysts (Kumar et al., 2013).

Use of silver catalysts or supported gold catalysts in electrolyzers in which the electrodes are separated by a flowing liquid electrolyte, either alkaline or neutral, significantly increases the CO production rate to 150-450 mA/cm^2, while still maintaining Faradaic efficiencies of 60-98 percent (Verma et al., 2016; 2018). Although there will always be a trade-off between maximizing rate and energetic efficiency (see Glossary in Appendix A), the overpotentials for CO reduction using silver or gold catalysts are fairly low, which means that rates of 150 mA/cm^2 can be achieved at energetic efficiencies exceeding 50 percent. In all these cases the oxygen evolution reaction takes place at the anode, typically using an IrO₂ catalyst. Based on these prior efforts that typically employ electrodes with a geometric area of 1-2 cm^2, Siemens performed experiments on a larger scale, using first 10 cm^2 and then 100 cm^2 gas diffusion electrodes in electrolyzer configurations with a flowing liquid electrolyte (Jeanty et al., 2018). These cells were successfully operated for 200 hours using a neutral electrolyte at a rate of 150 mA/cm^2, with a Faradaic efficiency for CO formation of 60 percent. Subsequently, Siemens collaborated with Evonik to connect their 10 cm^2 CO₂-to-CO electrolyzer (running at 300 mA/cm^2 for over 1,200 hours) with a fermentation process in which the formed CO is combined with unreacted CO₂ to form butanol and hexanol, at close to 100 percent Faradaic efficiency (Haas et al., 2018). Detailed economic analysis of this hybrid system highlights the promise for sustainable production of first CO and then other chemicals at scale using this approach.

In addition to low-temperature and high-temperature electrochemical cells described in the chapter, intermediate-temperature carbon dioxide electrolysis, with cell temperatures ranging from 200ºC to 500ºC, is a possible new direction that could provide access to products that are not made efficiently at either temperature extreme currently.

While these electrolyzer systems exhibit encouraging performance levels for the reduction of CO_2 to CO, the use of gas diffusion electrodes, especially in combination with an alkaline electrolyte, can cause problems. Typically, CO₂ flow rates that greatly exceed

the rate of CO_2 reduction are used to maximize the current density and Faradaic efficiency, which results in product streams that are diluted with a large excess of CO_2 (e.g., 3:1 CO_2:CO in the Siemens example above). In addition, some of the CO_2 is lost by diffusion through the gas diffusion electrodes into the electrolyte, where it can react with OH^- to form carbonates, which can precipitate on the electrode or migrate to the anode and release CO_2 into the O_2 stream. The rate of these undesired processes (often completely ignored in CO_2 electrolysis work) depends on the specific gas diffusion electrode used, the nature of the catalyst layer, as well as the flow rates and pressures of the CO_2 feed and the electrolyte. Achieving high CO_2 conversion with minimal loss of CO_2 into the electrolyte will be critical for advancing CO_2 electrolysis technology.

Dioxide Materials has reported a different electrolyzer configuration: an anion-conductive membrane-based electrolyzer with a silver cathode catalyst that sustains CO production rates in the range 100-200 mA/cm^2 over more than 1,000 hours (Kutz et al., 2017). The use of a membrane as the electrolyte between the electrodes significantly reduces some of the aforementioned issues (CO_2 loss and electrolyte degradation) associated with the use of liquid electrolytes. In recent collaborative work Dioxide Materials and 3M explored the electrochemical generation of syngas from water and CO_2, either (1) by operating a flowing liquid-electrolyte CO_2 electrolyzer cell for CO production and a polymer electrolyte-based water electrolyzer for H_2 production in parallel, or (2) by performing co-electrolysis of CO_2 and H_2O in a single anion-exchange membrane-based electrolyzer (Liu et al., 2016). Both systems produced CO and H_2 at industrially relevant rates (for example, CO_2 to CO at 100 mA/cm^2). The various technoeconomic analyses reported to date suggest that the electroreduction of CO_2 to CO has promise to become economically feasible.

Remaining challenges for electrochemical conversion of CO_2 to CO include (1) achieving sufficient stability and durability for both catalysts and electrodes, (2) the need to develop strategies that minimize loss of CO_2 to the electrolyte, and (3) the need to further reduce the overall energy requirement under operating conditions at practical CO production rates.

Ethylene and Ethanol Production

Ethylene is a high-volume commodity chemical that is used to produce a large number of other chemicals and is an important monomer in a range of different polymers. In 2016, over 150 million tons of ethylene were produced, almost exclusively from fossil fuel–derived precursors. Although the conversion of CO_2 to ethylene requires a large energy input, the prospect of using CO_2 as a carbon source for a large fraction of commodity chemical production has motivated many research efforts. One potential strategy is to hydrogenate CO_2 to ethylene, using a low-carbon source of H_2. Recent studies have described iron catalysts with promising selectivity for CO_2 hydrogenation to ethylene

and other light olefins (up to 65 percent) (Satthawong et al., 2015; Wang et al., 2013). However, these systems operate at low CO_2 conversion and also produce lower-value chemicals such as CO and methane, along with alkanes. At this stage a significant amount of catalyst improvement is required to develop systems which generate ethylene in higher yields. A more realistic short-term goal is the development of systems for the production of a mixture of hydrocarbons (Fischer-Tropsch chemistry) from CO_2 (see below).

Another route to ethylene production from CO_2 is electroreduction using copper catalysts. This reaction requires a significantly larger overpotential than CO_2 reduction to CO using gold or silver catalysts. Extensive investigations of different copper nanostructures and operating conditions have led to systems that produce ethylene, but achieving selectivities exceeding 40 percent has been difficult. Strategies such as alloying silver with copper, in which the silver enhances formation of the needed CO intermediate (Hoang et al., 2018), and precise engineering of the copper catalyst layer inside a sandwich-type gas diffusion electrode have increased Faradaic efficiencies for ethylene to 60-70 percent at rates of 160 to 250 mA/cm^2 (Dinh et al., 2018). Often a sizeable amount of ethanol (Faradaic efficiencies of 10 to 30 percent) is co-produced with the ethylene. Co-production of ethylene and ethanol—a valuable commodity chemical itself (with an annual global production of approximately 80 million tons in 2016)—may bring economic feasibility for ethylene production closer as a result of the additional income generated from the produced ethanol. Additionally, given that ethylene is a gas and ethanol is a liquid, separation of the products should be relatively straightforward, although extracting ethanol from the electrolyte may be challenging. In related chemistry, a promising class of boron- and nitrogen-co-doped nanodiamond catalysts was reported, which can achieve Faradaic efficiencies for ethanol production as high as 93 percent (Yanming et al., 2017). It is unclear whether this catalyst can be integrated on a gas diffusion electrode in a liquid electrolyte or membrane-based electrolyzer in order to achieve practical production rates.

Despite the progress in the electroreduction of CO_2 to ethylene (and ethanol), a large number of challenges remain. The few studies that have explored the stability of the various copper catalysts suggest that catalyst degradation and remodeling is a serious issue. Indeed, sustained operation of an ethylene-producing electrolyzer for more than 2 hours has not been demonstrated. Furthermore, as described above, loss of CO_2 to the electrolyte has the potential to be a major drawback. Despite these challenges, the prospect of converting CO_2 into a valuable and versatile chemical such as ethylene using low-carbon electricity is a powerful reason to continue to develop better and more durable catalysts, electrodes, and electrochemical cell designs.

Dimethylcarbonate and Diphenylcarbonate Production

Dimethylcarbonate is used to synthesize polycarbonates, as a mild methylating agent in organic chemistry, and as a solvent (Ma et al., 2009). It is currently produced on a

scale of 90 kilotons per year. Potential applications for dimethylcarbonate also exist in the fuel industry where it could be blended with gasoline as an oxygenate. Historically, dimethylcarbonate was synthesized from phosgene and methanol, but now it is prepared either via transesterification of ethylene carbonate or propylene carbonate and methanol or using CO, methanol, and O_2 as feedstocks. There has been considerable research into the development of catalysts for the conversion of CO_2 and two equivalents of methanol into dimethyl carbonate and water (Tamboli et al., 2017). Both homogeneous catalysts based on tin and heterogeneous catalysts based on ceria-zirconia oxides are capable of promoting the reaction. However, unfortunately, the thermodynamics for dimethylcarbonate formation from CO_2 are limiting and under standard reaction conditions (160-180°C, 90-300 atm CO_2), yields range between 1 and 5 percent. Although more advanced catalysts would be beneficial the crucial challenge for development of practical systems for dimethylcarbonate production is to discover cost-effective strategies for the removal of water to drive the equilibrium and increase the yields of dimethylcarbonate. An alternative strategy to make dimethylcarbonate from CO_2 involves using urea as a CO_2 carrier (Shukla and Srivastava, 2017). In this approach, the reaction of urea and methanol generates dimethylcarbonate and ammonia. The ammonia can then in principle be recycled back into urea through a reaction with CO_2. A number of catalysts are known for the conversion of urea and methanol into dimethylcarbonate and ammonia, and yields of up to 50 percent have been reported. However, improvements in selectivity are required, as well the developments of methods to remove ammonia as it is formed, as this will assist in driving product formation.

Diphenylcarbonate is used as a feedstock for the synthesis of aromatic polycarbonates and is produced on a 250 kiloton scale each year (Gong et al., 2007). It is prepared either using toxic phosgene and phenol or via the transesterification of dimethylcarbonate. Therefore, if a CO_2-based route for the synthesis of dimethylcarbonate is developed it will likely also lead to an improved method from the production of diphenylcarbonate. This is supported by the recent development of an indirect method to produce diphenylcarbonate from CO_2 and phenol by Asahi Kasei. The first step in the process is the reaction of CO_2 with n-butanol to generate di-n-butylcarbonate. Subsequently, the di-n-butylcarbonate is treated with phenol to generate diphenylcarbonate and n-butanol, which is recycled. To date, a 1,000 tons/yr facility has been operational for more than 1,000 hours. The direct synthesis of diphenylcarbonate from phenol and CO_2 is also possible but suffers from similar problems to the reaction of methanol with CO_2. In 2011, Shell opened a 500 ton per annum demonstration plant for the synthesis of diphenylcarbonate from phenol and CO_2 using propylene oxide as a water scavenger. In this reaction propylene glycol is also generated. Nevertheless, this method for the synthesis of diphenylcarbonate has yet to be used on a larger scale and is limited by the market for propylene glycol.

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Polymer Production

Plastics such as polycarbonates and polyurethanes have a wide range of applications ranging from insulating electronic components to cushioning materials (Qin et al., 2015). Petroleum is the key feedstock for the synthesis of most plastics. Replacing petroleum feedstocks with CO_2 could be desirable for both economic and environmental reasons and could also lead to biodegradable polymers with novel properties. CO_2 can be used as either a direct or indirect feedstock for the synthesis of polymers. In the direct approach CO_2 is used as a monomer unit, which is directly incorporated into the polymer. In the indirect approach CO_2 is first converted into a different monomer, for example, methanol, organic carbonates, carbon monoxide, ethylene, dimethylcarbonate, or urea, which is then polymerized. Other sections in this chapter evaluate the feasibility of CO_2 conversion into chemicals such as methanol, so this section will focus on the direct use of CO_2 in the synthesis of polymers.

Polycarbonates—plastics which contain carbonate groups—are typically synthesized through the reaction of phosgene with 1,2-diols (Lu and Darensbourg, 2012; Poland and Darensbourg, 2017; Qin et al., 2015). The copolymerization of CO_2 with epoxides to produce polycarbonates is an alternative synthetic route. Numerous heterogeneous and homogeneous transition-metal catalysts have been developed which selectively form polycarbonates as opposed to the cyclic carbonates described earlier (see the section "Commercial Technologies for the Chemical Utilization of Methane" in Chapter 6) from a range of comonomers including ethylene oxide, propylene oxide, cyclohexene oxide, vinyl oxide, and styrene oxide, among others (Lu and Darensbourg, 2012; Poland and Darensbourg, 2017; Qin et al., 2015). Typically homogeneous catalysts are preferred because they give higher selectivity. Additionally, by changing the nature of the catalyst, polymers can be produced which are either alternating and contain only carbonate groups (one molecule of CO_2 followed by one molecule of epoxide) or statistical (often referred to as polyether carbonates) and contain ether linkages that are formed when two ring-opened epoxides are adjacent to each other.

In general, alternating copolymers have low glass transition points, meaning that they will only be used in niche applications such as binders in ceramics and adhesives (Qin et al., 2015). Nevertheless, Empower Materials currently sells poly(ethylenecarbonate) made from ethylene oxide and CO_2, and Econic manufactures polycarbonates that contain up to 50 percent CO_2 by weight (Quadrelli et al., 2011). A problem which companies such as Novamer are trying to address is the tendency of the polycarbonate to decompose to the cyclic carbonate, especially when electron-deficient epoxides are used. Both this problem and the tendency of polycarbonates with high CO_2 content to react with water can in principle be solved through the judicious use of additives but this still needs to be studied further. At this stage research is also still required to develop catalysts that are highly active with a wide range of epoxides, which may lead to alternating polymers with higher glass transition temperatures. Additionally, further development of strategies to incorporate

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another monomer like cyclohexene oxide into the copolymer to improve the properties of the polymer should be pursued. The reaction of CO_2 with epoxides is highly exothermic so finding catalysts that are thermally stable is also a key issue.

In contrast to the limited applications for alternating copolymers, polyether carbonates derived from epoxides and CO_2 are useful for a much wider range of applications (Qin et al., 2015). In particular, they can be used as a component in polyurethanes, and, apart from the commercial application described in the Introduction to this chapter, Novomer and Covestro are both selling polyether carbonates for use in polyurethane synthesis. Nevertheless, despite the relative maturity of this field there is still room for growth. Further understanding of how catalyst structure effects polymer properties would be useful, as this could lead to the development of polymers with tailor-made structures.

Recently research has begun on using epoxide starting materials which are derived from renewable feedstocks such as cyclohexadiene oxide, limonene oxide, and α-pinene oxide, and catalysts have been developed for the copolymerization of CO_2 with these substrates (Poland and Darensbourg, 2017). This is a promising area and further research to develop more efficient catalysts should be performed. Additionally, research into the copolymerization of CO_2 with aziridines to produce polycarbamates and oxetanes is also only at an early stage and should also be encouraged as it may lead to polymers with different properties than those currently available.

Carboxylic Acid Production

Carboxylic acids comprise a broad class of commodity chemicals that are used as solvents, reagents, and monomers for polymer production, among other applications. With the exception of acetic acid, which is made by methanol carbonylation (Sunley and Watson, 2000), commodity chemical–scale carboxylic acids are typically synthesized by aerobic oxidation of hydrocarbons. Although these processes have been optimized over many years, they generally require highly corrosive conditions that necessitate expensive reactors. Conceptually, inserting CO_2 into a C–H bond is an attractive alternative synthesis of carboxylic acids that would eliminate the need for a difficult oxidation step. However, CO_2 insertion is thermodynamically disfavored by ~10-18 kcal mol^{-1} depending on the type of C–H bond (it is both endothermic and entropically disfavored). As a result, catalytic reactions either need to be performed in the presence of base (to drive the reaction forward by carboxylate formation) or need to be combined with a very effective separation process to remove the carboxylic acid in situ. The vast majority of research focusing on the preparation of carboxylic acids from CO_2 insertion has focused on the former. Another major challenge is the kinetic difficulty of activating C–H bonds in the absence of a strong oxidant. Researchers have typically resorted to the use of highly reactive, resource-intensive reagents (e.g., strong organic bases, Lewis acids, and zero-valent metals) to

overcome this barrier, which renders these methods impractical. Even though research into the production of carboxylic acids from CO_2 is still in an early stage, the large number of potential applications of carboxylic acids motivates further efforts. Below, an assessment is provided about the current state of research toward a number of carboxylic acid targets.

Acrylic and Methacrylic Acid Production

Acrylic acid (5.8 million tons were produced in 2014; Limbach, 2015) and methacrylic acid (3 million tons of methyl methacrylate, the methyl ester of methacrylic acid, were produced in 2007) are large commodity-scale chemicals used in the synthesis of polymers and water superabsorbers (Limbach, 2015). Acrylic acid can also be converted into acrylonitrile, which is a feedstock for carbon fiber synthesis. The current production of acrylic acid and methacrylic acid from petrochemical starting materials leaves open opportunities to use CO_2 as a more sustainable feedstock. In principle, acrylic acid and methacrylic acid could be formed directly from CO_2 insertion into a C–H bond of ethylene or propylene, respectively (Limbach, 2015). As noted above, the thermodynamics of these processes are unfavorable, which has led to a stepwise approach in which the carboxylate is formed first and subsequently protonated in a second step. Research into the development of catalysts for the synthesis of acrylate (the deprotonated form of acrylic acid) has primarily focused on homogeneous systems and is still at a very preliminary stage. State-of-the-art methods utilize Pd and Ni catalysts, an organic base (amine or alkoxide), and a stoichiometric amount of a Zn^0 promoter to convert ethylene and CO_2 into acrylate with low turnover frequencies (<0.1 h^{-1}) and turnover numbers less than 1,000 (Hendriksen et al., 2014; Limbach, 2015; Stieber et al., 2015). A viable CO_2 route to acrylic acid will require much more development to improve the catalyst performance, eliminate the requirement for Zn^0, and engineer a process which can operate without a base or with efficient base recycling.

Furan-2,5-Dicarboxylic Acid Production

Furan-2,5-dicarboxylic acid (FDCA) is a monomer that has attracted strong commercial interest for polyester synthesis (Sousa et al., 2016). In particular, polyethylene furandicarboxylate, the condensation polymer of FDCA and ethylene glycol, has superior gas barrier properties to polyethylene terephthalate, which is produced on scale of 60 million tons per year (Pang et al., 2016). One potential method for FDCA synthesis involves edible fructose as a feedstock and requires difficult oxidation and purification steps. The carboxylation of furoic acid is potentially an advantageous route because furoic acid is produced from furfural, which is made industrially from inedible biomass. Recently, researchers have reported that simple alkali carbonate salts (M_2CO_3; M^+ = alkali cation)

can promote CO_2 insertion into C–H bonds to form carboxylates under solvent-free conditions at elevated temperatures (200°C to 350°C) (Banerjee et al., 2016). This chemistry was used to convert furoic acid and CO_2 into FDCA in high yield on a 1 mol scale (Dick et al., 2017). The absence of transition-metal catalysts allows for the use of relatively low-purity CO_2 (industrial grade). Nevertheless, using carbonate-promoted carboxylation for commodity chemical synthesis will require substantial development to increase the reaction rates and integrate the process with efficient methods to regenerate carbonate.

Benzoic Acid Production

Benzoic acid is a relatively small-scale commodity chemical (600,000 tons per year) used as an intermediate in phenol synthesis and in the production of preservatives (alkali benzoates), plasticizers (benzoate esters), and solvents. Currently, benzoic acid is synthesized industrially through the aerobic oxidation of toluene. The preparation of benzoic acid by inserting CO_2 into a C–H bond of benzene has been investigated as an alternative strategy in a few early stage research efforts. These methods have relied on very energy-intensive stoichiometric reagents to activate benzene, such as $Al_2(CH_3)_3(OCH_2CH_3)_3$ or a combination of $AlCl_3$ and Al^0 (Olah et al., 2002; Suga et al., 2014). While these examples have provided insight into chemical strategies for activating aryl C–H bonds, the CO_2 footprint associated with the production of strong Lewis acids far outweighs the CO_2 consumed in the benzoic acid synthesis. Further research is needed to uncover strategies for avoiding stoichiometric reagents altogether.

Oxalate and Oxalic Acid Production

Oxalates and oxalic acid, while not commodity chemicals, are still produced at a scale of 120,000 tons per year (Qiao et al., 2014). Their synthesis normally involves the reactions of alcohols with CO and O_2 to form diesters of oxalic acid, which can be hydrolyzed with acid to give oxalic acid. This is a relatively cumbersome process. If efficient and economical methods to convert CO_2 into oxalic acid are developed, the amount of oxalic acid produced may increase dramatically, as oxalic acid represents a convenient feedstock for the synthesis of a range of chemicals. For example, there are commercial processes for the conversion of dimethyl oxalate into monoethylene glycol. Currently, dimethyl oxalate is made from CO and H_2, but the esterification of oxalic acid made from CO_2 may represent a more sustainable process. Liquid Light (now owned by Avantium) developed a process for the synthesis of ethylene glycol through the initial electrochemical conversion of CO_2 to oxalic acid (Table 4-2), which is then converted into ethylene glycol using standard chemistry (Twardowski et al., 2016).

Researchers continue to work on more efficient methods to synthesize oxalates and oxalic acid from CO_2. In early research (prior to 2000), Pb and other catalysts were used to generate oxalic acid in electrochemical cells with Faradaic efficiencies in the 70-98 percent range, but this was only done at low rates in a standard electrochemical cell (Rudolph et al., 2000; Shoichiro et al., 1987). More recently, both mononuclear and binuclear copper complexes have shown promise for electrochemical reduction of CO_2 to oxalic acid (Angamuthu et al., 2010; Pokharel et al., 2014). Nevertheless, further mechanistic understanding of this process is required to lower the overpotential and to improve selectivity.

Fuel (Hydrocarbon) Production

Given that the majority of CO_2 that is released in the atmosphere is from the combustion of fossil fuels, the development of methods to synthesize fuels from CO_2 could result in a closed carbon cycle, where increases in concentration of CO_2 in the atmosphere will be minimal. This can only be achieved if the electricity or H_2 that is used to reduce CO_2 is generated from carbon-free sources, and if the carbon waste gases created by the combustion of the fuel are recaptured and reutilized. In principle, methane and methanol could be used as fuels and as discussed earlier systems for the conversion of CO_2 into these molecules are actively being pursued. Therefore, in this section only the state of technology for the conversion of CO_2 into hydrocarbon fuels with more than two carbons will be described.

The Fischer-Tropsch process is used to convert CO and H_2 into liquid fuels and has been commercialized on a large scale (Artz et al., 2018) In addition to large-scale units for Fischer-Tropsch, smaller units, which may be better suited for use with waste carbon streams, are also being developed. In an earlier section of this chapter methods for the conversion of CO_2 to CO were described. One approach for producing fuels from CO_2 could involve initially electrochemically synthesizing CO from CO_2 and then in a second thermal step combining the CO with sustainably produced H_2 to produce fuels via the conventional Fischer-Tropsch process. Alternatively, a significant amount of research is currently being performed to develop systems that can perform Fischer-Tropsch chemistry starting from CO_2 in a single reactor using a single catalyst. In this chemistry the first step is generally the reverse water gas-shift reaction to generate CO from CO_2 (Eq 1). This CO then reacts with H_2 to form liquid fuels through a mechanism based on the conventional Fischer-Tropsch reaction (Eq 3). Both Sunfire and INERATEC have developed small-scale demonstration plants for CO_2-based Fischer-Tropsch chemistry (Table 6-2). However, these rely on water electrolysis to supply H_2, which is not economically competitive on a large scale. One of the challenges associated with the Fischer-Tropsch process using CO_2 is that there is only a small concentration of CO present during the reaction. This limits chain growth and consequently the product distribution is normally rich in light

hydrocarbons, which are not suitable as liquid fuels. To date, iron-based catalysts, which are active for both the reverse water gas-shift reaction and Fischer-Tropsch chemistry, have been the most extensively explored (Wei et al., 2017). Various transition metal–based promotors have been added to iron-based catalysts and give improved product distributions, but further research to understand the mechanism by which these operate is required. Similarly, supporting catalysts on materials such as SiO_2 gives improved performance, but there is relatively little understanding of these effects. Further research into the development of new catalysts and the optimal design of reactors is likely to result in even better systems, given the relatively early stage of research in this field.

The electroreduction or photoreduction of CO_2 to chemical fuels has also attracted significant research interest (Ganesh, 2016; Lim et al., 2014; White et al., 2015). Although most commonly CO_2 is reduced to C_1 feedstocks such as CO, formic acid, methanol, or methane, there are a number of systems that can form products containing new carbon-carbon bonds. In particular copper catalysts are effective for forming products containing C–C bonds such as ethylene (see above), ethane, and higher-order hydrocarbons (Ren et al., 2015a). Apart from selectively forming C_2 or higher products over C_1 products the other major challenge in electrochemical CO_2 reduction to fuels is inhibiting the hydrogen evolution reaction which produces H_2 as a by-product. At this stage there is also a lack of mechanistic information about the elementary processes which facilitate C–C bond formation and further research on this topic would likely be beneficial. There is still significant room to design tailor-made catalysts for electrochemical CO_2 reduction and even though this problem is extremely challenging it is likely that further advances can be made.

Carbon Nanotube Production

The controlled synthesis of carbon nanotubes is a relatively recent discovery, which has already led to the commercial application of nanotubes in sports gear, such as bicycles and skis, boat hulls, and water filters (De Volder et al., 2013). In fact, as a result of their unusual thermal conductivity, mechanical, and electrical properties, there are many potential applications for carbon nanotubes. However, the preparation of carbon nanotubes is relatively expensive, which limits potential uses, and the current market size is small. Carbon nanotubes are typically produced using CO from fossil feedstocks as the carbon source. Recently, it has been demonstrated that carbon nanotubes can be produced electrochemically from CO_2 (Licht et al., 2016; Ren et al., 2015b). The process, which to date has only been performed on a laboratory scale, involves molten carbonate electrolysis in the presence of CO_2. Specifically, molten Li_2CO_3 can be reduced to generate carbon nanotubes and Li_2O. The Li_2O then reacts with CO_2 to regenerate Li_2CO_3, meaning that CO_2 is the ultimate carbon source for the nanotubes. Although carbon nanotubes are a valuable item, at this stage their range of applications is limited compared to conventional

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carbon fibers. The carbon nanotubes that have been produced from CO_2 to date do not have suitable properties to act as replacements for the types of carbon fibers which are used extensively in the aerospace and automotive industry (Rahaman et al., 2007). However, if methods can be developed to produce more widely useful carbon nanotubes or carbon fibers from CO_2, this has the potential to be a disruptive technology.

INTERSECTING RESEARCH CHALLENGES FOR CO₂ CONVERSION

The section above describes the status of technology and research related to CO_2 conversion separated by product type and identifies some of the challenges that need to be addressed to develop improved systems. A summary of the key technological barriers for different products is provided in Table 4-3. Although in some cases the problems are specific to a certain product, some challenges are common to a number of different products. In this section, some of these common challenges associated with developing improved systems for CO_2 conversion are discussed.

Challenges in Catalyst Development

As described above, many catalysts for the conversion of CO_2 into valuable chemicals have been developed. Although in some cases there are reasons specific to a particular product for why these catalysts are not commercially viable, in general, catalysts for CO_2 conversion lack the required durability and stability. Even in cases where turnover frequencies are high, catalyst decomposition is a problem. This challenge is perhaps even more severe than realized, as most systems tested on a small scale use purified CO_2. If these catalysts were utilized with nonpurified CO_2 they could decompose even more rapidly. Purifying CO_2 increases the cost of a process, and the development of systems that are compatible with CO_2 which contains the type of impurities present in flue gas would make commercialization easier. Similarly, the utilization of CO_2 from gaseous waste streams would be aided by improving the interface between CO_2 capture and conversion. There are relatively few catalysts for CO_2 conversion which have been utilized in conjunction with systems for CO_2 capture and this could play a key role in developing efficient approaches to utilize CO_2 from waste streams.

Challenges for Low-Temperature Electrochemical CO₂ + H₂O Conversion

Electrochemical CO_2 conversion is appealing because it could be powered directly by renewable electricity sources. As noted in Chapter 7, increased deployment of low-carbon electricity generation from solar and wind has, at certain locations and times, led

electricity prices to decrease to zero or negative values, indicating a possible future with greater incentive for utilization of renewable electricity. Most of the activity in this area has focused on electrochemical systems in which CO_2 reduction to a C_1 or C_2 chemical intermediate is coupled to water oxidation to O_2 (oxygen evolution reaction). The overall process is effectively the combustion reaction in reverse, with electric power providing the energy input. Although significant progress has been made in this area over the past 10 years, multiple interrelated technical challenges remain—challenges that must be addressed to allow for practical devices.

Enhancing Conversion per Pass and Avoiding Carbonate Formation

The development of an effective cathode for CO_2 reduction is a major obstacle that has captured much of the attention in this area. An ideal cathode will reduce CO_2 to a single desired product at a high rate with minimal overpotential and maintain its activity for long periods of continuous operation. Some systems capable of these transformations are described above. High synthesis rates require effective mass transport of CO_2 to the catalyst material while maintaining high ionic conductivity. These requirements have been met by using gas diffusion electrodes, which are used in commercial technologies such as fuel cells and electrolyzers. As summarized in preceding sections of this chapter, electrolysis cells employing gas diffusion electrodes have been used successfully for electroreduction of CO_2 to products such as formic acid, CO, and ethylene at potentially commercially relevant rates exceeding 100 mA cm^{-2}. Most of these flow electrolysis systems, however, are operated such that (1) only a modest percentage of CO_2 (1-20 percent) is converted to the desired product, that is, a low single-pass conversion, and (2) some of the CO_2 is captured by OH$^-$ in the electrolyte to form carbonate. A low single-pass conversion implies that more energy will be needed to separate gaseous products from the product stream, and to recycle the unreacted CO_2 back into the feed. Second, formation of carbonates represents a net loss of CO_2 and causes electrolyte degradation and electrode performance degradation (carbonate precipitation). Given the energy required to obtain CO_2 of sufficient purity to begin with, low CO_2 utilization per pass and loss of CO_2 in the electrolyte imposes additional energy penalties that are typically not accounted for in system analyses. In fact most experimental work reported does not explicitly acknowledge, let alone quantify, these parasitic losses. Achieving practical electrochemical systems for conversion of CO_2 to valuable intermediates such as CO and ethylene requires the development of systems that achieve high single-pass conversion of CO_2 to the desired product with minimal loss of CO_2 into the electrolyte.

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Energy Requirements of the Anode

Another key factor to make the overall electrolysis process (more) economically feasible is to enhance energy efficiency and minimize overall energy requirements in order. Some gains can still be made by reducing the overpotential of the various cathode catalysts. However, those potential gains are small compared to the energy requirements of an overall electrolysis process that typically couples the CO_2 electroreduction at the cathode to the highly energy intense oxygen evolution reaction (OER) at the anode. An analysis of the energy requirements based on only Gibbs free energies shows that about 90 percent of the energy needed to drive the CO_2 electrolysis process is required for OER at the anode, to form O_2, for which there is very limited commercial value at scale. Indeed efforts have started to identify alternative anode reactions that involve the oxidation of readily available chemicals. For example, glycerol (a by-product of biodiesel production), glucose, and even methane, for which the thermodynamic potentials are 0.8-1.1 V lower than the minimum potential needed for the OER, have potential in this regard. In fact, it has been demonstrated that glycerol oxidation can lead to a 37-50 percent reduction in the energy requirement for the overall CO_2 electrolysis process, and with the cost of electricity often the prime cost-determining factor (Jouny et al., 2018), this significantly changes the likelihood of achieving economic viability. Of course, no chemical is as abundantly available as water for the OER; however, vast amounts of (waste) chemicals like glycerol are available in various places around the world, for example, in Brazil's biofuel production. In those locations CO_2 electrolysis to CO, ethylene, and/or ethanol has the potential to become a viable technology when coupled with glycerol oxidation.

A RESEARCH AGENDA FOR CHEMICAL UTILIZATION OF CARBON DIOXIDE

Stages of development and key barriers for various chemical utilization approaches are shown in Figure 4-1 and Table 4-3.
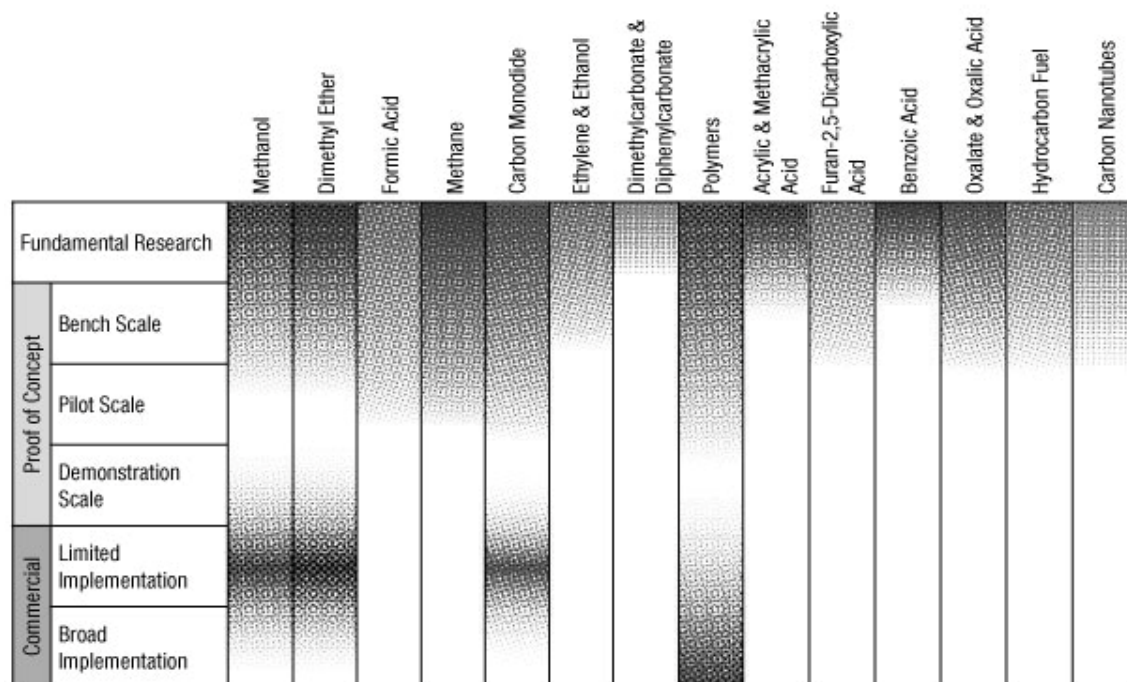
FIGURE 4-1 Stages of research activity for target products of carbon dioxide waste stream chemical utilization. The higher density on the diagram indicates larger amounts of research activity in that stage. Blank areas indicate little or no research activity in that stage for a given product, indicating gaps in research activity.

NOTE: Fundamental research is defined as observation and reporting of fundamental principles of a scientific or engineering process, and formulation of a technology concept. The three proof-of-concept stages are defined as progressively larger-scale reactions to produce product. These include bench-scale processes where critical functions are proved and components or systems are validated in a laboratory environment and at a laboratory scale. Pilot plant scale is defined as a system validated in a relevant environment and at an engineering scale. Demonstration plant scale is defined as a full-scale system demonstrated in a relevant environment. Commercial-limited is defined as an actual system operating at a stage where product is being sold in the market in limited areas with specific advantageous geographical, regulatory, or other factors. Commercial-broad is defined as an actual system operating at a stage where product is sold in the market with opportunities not limited to specifically advantaged locations.

TABLE 4-3 Key barriers for commercialization of the products from Figure 4-1.

Product	Key Barriers
Methanol	• Direct hydrogenation of CO_2: low selectivity, catalyst inhibition by water • Electroreduction of CO_2 in water: high overpotentials, low selectivity
Dimethyl Ether	• Similar challenges to methanol production
Formic Acid	• Homogeneous hydrogenation of CO_2: stoichiometric added base required for high turnover, separation of formic acid from reaction medium/base recycling • Photoelectrochemical and electrochemical reduction of CO_2: poor catalyst stability, separation of formic acid from reaction medium
Methane	• Electroreduction of CO_2: very high overpotentials, low selectivity
Carbon Monoxide	• Electroreduction of CO_2: High flux of CO_2 to cathode required, low per-pass conversion.
Ethylene and Ethanol	• Electroreduction of CO_2: low selectivity, poor catalyst stability
Dimethylcarbonate and Diphenylcarbonate	• Alcohol/CO_2 condensation: low per-pass conversion • Alcohol/urea condensation: low selectivity, low per-pass conversion
Polymers	• Polycarbonates: tendency of product to decompose into cyclic carbonates; high-purity CO_2 required • Polyether carbonates: understanding catalyst structure–polymer property relationship for tailored products
Acrylic and Methacrylic Acid	• Very low catalyst turnover frequencies; requirement for stoichiometric additives
Furan-2,5-Dicarboxylic Acid	• Low reaction rates, salt recycling process for carbonate regeneration not proven on large scale
Benzoic Acid	• Requirement for stoichiometric additives
Oxalate and Oxalic Acid	• High overpotential, low selectivity
Hydrocarbon Fuel	• Low selectivity, lack of understanding of carbon-carbon bond formation steps
Carbon Nanotubes	• Properties of currently produced carbon fibers not suitable to act as replacements for carbon fibers

Priority Research Areas

In previous sections of this chapter specific challenges related to converting CO_2 to certain products, general challenges related to CO_2 conversion regardless of the product, and the technological barriers to commercialization have been described. Based on the findings of these sections, a general list of scientific research needs and opportunities related to the conversion of CO_2 to commodity chemicals and fuels is provided below.

Chemical Catalysis

Both in the short and long term there is a need for improved catalysts for CO_2 conversion. Depending on the application, this could include homogeneous, heterogeneous, and electro- and photochemical systems. Where possible, an emphasis placed on developing catalysts that use sustainable raw materials would be beneficial. Additionally, catalyst stability and durability need to be improved for many CO_2 conversion technologies.

Avoiding Stoichiometric Additives

Many current processes for CO_2 conversion, especially in academic settings, use stoichiometric amounts of additives (such as base). Although these additives are sometimes required for thermodynamic reasons, they limit atom economy, generate waste products, and increase the net carbon footprint of the process. Research focusing on developing systems which can use catalytic quantities of additives instead of stoichiometric amounts or removing additives altogether through the use of reactors that allow reactions to be performed at low conversion should be encouraged.

Integrating Catalysis and Reactor Design

When using waste CO_2 as a feedstock, catalysts need to be compatible with the impurities present in the waste stream and able to operate with the concentration of CO_2 in waste stream, or the waste gas needs to be concentrated and/or purified. Research into interfacing systems for CO_2 conversion with capture technology is required. This includes both chemical and reactor design considerations. Alternatively, the development of catalysts that can react directly with captured CO_2 (for example, CO_2 which has been captured using an amine) should be explored further.

Pathways to New Products

Research exploring CO_2 conversion into commodity chemicals has traditionally focused on a relatively small number of molecules, as outlined in this chapter. Most of these tend to be C_1 products. Recent efforts to make molecules such as ethylene or materials such as carbon nanotubes from CO_2 represent departures from the norm. The

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identification of other nontraditional targets and subsequent catalyst development could have transformative impacts.

Coupling Oxidation and Reduction Reactions

The focus of most CO_2 electroreduction efforts has been on improving the cathode in its efficiency and activity in converting CO_2 to a desired product. Typically the overall process requires stoichiometric amounts of water for the oxygen evolution reaction on the anode, with that reaction requiring more than 85 percent of the total electrical energy input. Though O_2 will in some cases be a valuable co-product, at scale, the amount of produced oxygen is likely to vastly exceed need, and thus the produced oxygen would be released. Converting some other feed into a valuable product at the anode, which at the same time would reduce the anode's energy requirement, would significantly improve the overall economic feasibility and life-cycle assessment of CO_2 electrolysis.

System Engineering and Reactor Design

Improving the efficiency of CO_2 conversion chemistry would be aided by the integration of catalysts with the most efficient reactor technology. For example, the integration of CO_2 conversion catalysts with reactors that allow for the efficient removal of products that must be formed at low conversion for thermodynamically limited reactions would be beneficial. Similarly, separation challenges can be mitigated by developing reactor designs that improve conversion per pass. In electrochemical CO_2 conversion, developing improved membrane-based electrolyzers instead of liquid electrolyte-based electrolyzers should be a goal. Furthermore, integrating catalyst into durable electrode configurations, while still maintaining catalyst activity, will need further attention. To achieve these important objectives chemists and engineers should be encouraged to collaborate to jointly solve problems and develop new processes.

FINDINGS, CONCLUSION, AND RECOMMENDATIONS

Finding 4-1 At present, there are very few industrial processes that convert CO_2 into fuels or chemicals.

Finding 4-2 Most of the research and development of CO_2 utilization processes has targeted C_1 compounds (methane, CO, methanol, and formic acid) with a few prominent exceptions such as organic carbonates and polymers. Processes that produce compounds with C–C bonds have received less attention and are at an earlier stage of development.

Finding 4-3 Catalyst performance is a limiting factor in many CO_2 conversion processes. There is a substantial need for improved heterogeneous, homogeneous, and (photo)electrochemical catalysts. Major

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challenges include minimizing the energy input required for CO_2 conversion and improving catalyst selectivity, stability, and tolerance to common impurities in waste CO_2 streams.

Finding 4-4 Research on catalysts for CO_2 conversion is often conducted using reactors and reaction conditions (e.g., single-pass conversion) that are not suitable for the economic large-scale synthesis of chemicals or fuels at reasonable rates. The factors that affect catalyst performance in simplified laboratory reactors may differ from those that affect performance in a reactor engineered for larger-scale and higher rates.

Finding 4-5 Many CO_2 conversion processes that have been investigated require stoichiometric additives that cannot readily be regenerated. This requirement likely precludes commodity chemical or fuel synthesis because such additives can have an economic value or energy demand that exceeds that of the chemical or fuel product.

Finding 4-6 In electrochemical CO_2 conversion, water oxidation to O_2 is typically used as the anodic reaction to supply the protons and electrons for CO_2 reduction. Although water is by far the most scalable substrate, processes that use alternative oxidation substrates (e.g., those derived from agricultural waste or industrial by-products) could allow for CO_2 conversion with lower energy demand and generate a more valuable co-product than O_2.

Conclusion 4-1 The grand challenge for converting CO_2 waste streams into useful products is to develop processes that require minimal amounts of nonrenewable energy, are economically competitive, and provide substantial reductions in greenhouse gas emissions compared to existing technology.

Recommendation 4-1 Researchers should continue research efforts to improve existing catalysts or discover entirely new catalysts to advance many CO_2 conversion processes to industrial viability.

Recommendation 4-2 Researchers should focus on CO_2 conversion processes that avoid stoichiometric additives or use additives that are easily regenerated for developing processes that could be used for commodity chemical or fuel production.

Recommendation 4-3 Researchers should integrate catalysis research with reactor design at an early stage to accelerate the development of CO_2 conversion processes by rapidly identifying the factors that affect catalyst performance on larger scales at synthetically relevant rates.

Recommendation 4-4 Researchers should increase attention to CO_2 conversion processes that produce nontraditional targets, especially those with C–C bonds, to have transformative impacts.

Recommendation 4-5 Researchers should explore processes that combine CO_2 reduction with the oxidation of substrates from other waste streams (e.g., agricultural or biomass waste or industrial by-products) to open new

pathways that would reduce the cost of CO_2 conversion and create multiple high-value products.

Recommendation 4-6 Researchers should develop reactor technologies that are tailored to the demands of carbon dioxide conversion processes, including systems that integrate capture with conversion.

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5

Biological Conversion of CO$_2$ into Chemicals and Fuels

Harnessing the natural ability of microorganisms to capture and convert CO$_2$ into chemicals and fuels has great potential for utilization of gaseous carbon waste. Because biological processes have unique carbon utilization resource requirements and product opportunities, these can be seen as complementary to chemical and mineral carbonation options. This chapter addresses opportunities, challenges, and research needs relevant to utilization technologies that convert CO$_2$ into various products through photosynthetic and nonphotosynthetic means.

PHOTOSYNTHETIC APPROACHES TO CARBON WASTE GAS UTILIZATION

Approaches Based on Algae

While nonphotosynthetic processes for carbon waste gas utilization can produce high biomass yields, these systems suffer from poor life-cycle analyses when compared to photosynthetic methodologies (Vieira et al., 2013). Among photosynthetic processes, algal biomass provides high yields, with more than 30- to 50-fold improvement in oil yield in comparison to common agricultural crops (Singh and Gu, 2010). The term algae broadly refers to any photosynthetic prokaryotic microorganism (cyanobacteria) or eukaryotic microorganism (microalgae) that can be cultivated. Algae cultivation was introduced in the 1950s and has been practiced both academically and commercially for decades (Fisher and Burlew, 1953; Golueke and Oswald, 1959). Algae can be viewed as self-replicating machines that convert sunlight and CO$_2$ into value-added products. Products of algae cultivation include a wide range of biofuels, dietary protein and food additives, commodities, and specialized chemicals.

Algal biofuels have long been seen as a potentially viable strategy for addressing dwindling petroleum reserves, and investments in algal biofuel technologies have tended to rise when crude oil prices rise. For example, the U.S. Department of Energy (DOE) Office of Fuels Development funded the Aquatic Species Program, focused on the production of biodiesel from microalgae, from 1978 to 1996 (Sheehan et al., 1998), and in 2008 DOE renewed its support for algal biofuel research after crude oil prices topped $100/barrel. This most recent spike in research investment coincided with large

investments in algal biofuel technologies by startups and established companies; however, a subsequent decrease in crude oil prices to below \$30/barrel in 2016 created a major setback to industrial efforts. There are a wide range of estimates for the cost of production for algal biofuels (NRC, 2012) and it is difficult to predict how future policy and other factors may influence their competitiveness with traditional fossil resources; however, one challenge of algal cultivation stems from the cost and development of infrastructure for physical processing, such as dewatering and extraction, that continue to pose challenges for energy demand (Sander and Murthy, 2010). One obstacle to the growth of these methods will be adoption of support and infrastructure commonly available to other forms of domestic agriculture (Trentacoste et al., 2015). Multiple reports describe the state of the science and research challenges for algal biofuels (DOE BETO, 2016, 2017; DOE EERE, 2010, 2017; NRC, 2012; Sheehan et al., 1998).

Algae cultivation offers significant productivity improvements as compared to contemporary agriculture. Multiple studies have demonstrated up to 30-fold productivity improvements in oil production (Abishek et al., 2014; Wen and Johnson, 2009) and 50-fold improvements in protein production from algae when compared to soybean, canola, or corn (Bleakley and Hayes, 2017) per acre of land. Although not fully evaluated, protein derived from algal biomass has been proposed for both animal and human consumption, and some companies, for example, Qualitas,[1] already produce specialized algae to enrich animal feeds. The competitive landscape for algal cultivation would shift should these commercial applications prove competitive with current agricultural products such as soy or corn.

Despite these advantages, there are also significant challenges to algae cultivation. Photosynthesis is inherently inefficient, as only 3-6 percent of total solar radiation energy is captured (Zelitch, 1975). In addition, a limitation of algae is the efficiency of the carbon dioxide conversion that limits the annual flux (Wilcox, 2012). To compensate for this low efficiency, cultivation ponds or bioreactors are often designed to maximize light exposure through large volume and surface area; as a result, algal cultivation can be land and water intensive. Theoretically, to capture all CO_2 from a 10 kiloton/day power plant would require 25-37 acres of cultivation (Hazelbeck, D., personal communication, 2018). In addition, biomass cultivation presents capital and operations costs that do not have close parallels in existing large-scale industries.

On the other hand, a key benefit to biological systems is their inherent flexibility in terms of feedstocks and environments. There are opportunities to utilize nonarable land and saline or waste water for algae cultivation, thereby minimizing competition for natural resources. In addition, biological systems can tolerate low CO_2 concentrations and impurities in the carbon sources common to industrial power generation. These variables have a considerable impact on capital and operations costs for biological conversion

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[1] See https://www.qualitas-health.com/.

technologies, and it is important to account for resource use and environmental impact when comparing algae cultivation to conventional agriculture or other activities.

Approaches Based on Green Algae

Green algae, a common term for eukaryotic single cellular photosynthetic organisms deriving from several phyla, are a highly diverse group of algae representing many thousands of identified species. Multiple strains have been validated in biomass applications, and their selection is commonly determined by culture conditions. For instance, algae from cold environments have adapted to these environments through modification of primary metabolism and physiology (Morgan-Kiss et al., 2006).

The majority of biomass cultivation efforts using green algae have focused on biofuel production. In addition, several co-products have been identified that can help make biofuel production more economically feasible. The following sections describe opportunities for using green algae to produce various biofuels and co-products, as well as opportunities and limitations involved in advancing such applications through genetic manipulation.

Biodiesel Production

Biodiesel, or fatty acid methyl ester, production from plant- and animal-based fats and oils (including those from green algae) is now considered part of a mature industry. While biodiesel can be used as drop-in diesel replacement in many diesel engines, its hygroscopicity, cloud point, and fouling properties have limited widespread adoption. Once considered an ultimate product of biomass production, biodiesel has more recently become relegated to small fuel markets and as an additive for ultra-low-sulfur petroleum diesel to provide added lubricity properties (Hazrat et al., 2015).

After biomass harvesting, lipids are extracted by one of several methods to prepare isolated neutral lipids, or triacylglyceride (TAG), or total lipids containing both polar and neutral lipids. The traditional process for biodiesel production from plant- and animal-based fats and oils typically requires a high-purity source of TAG; however, methods have been developed to produce biodiesels from total lipid extracts (Asikainen et al., 2015; Mubarak et al., 2015).

Renewable Diesel/Gasoline Production

The most broadly adoptable advances in algae biomass conversion to biofuels lies in the catalytic hydrogenation of lipid extracts, known as hydrotreatment, for the production of true diesel and gasoline components. Although the methods for these transformations have been known for decades, the capital infrastructure required to carry out hydrotreatment on a commercial scale has limited its implementation to a few refining companies, such as Neste Oil and Chevron (Al-Sabawi and Chen, 2012; No, 2014).

One particular benefit of renewable diesel and gasolines is the flexibility with regard to the source of feedstock. Currently, industrial hydrotreatment processing can utilize fats and oils from any bioderived triacylglyceride source, including vegetable oils and animal fats. However, while algal lipids do contain triacylglycerides, extracts from many species also contain significant portions of polar lipids and hydrophobic pigments. New technology may be required for conversion of these species into renewable fuels by hydrotreatment facilities (Davis et al., 2013). The requirement of hydrogen gas for the catalytic hydrogenation of lipid extracts must also be considered.

In addition, liquefaction, pyrolysis, and gasification offer routes to produce a variety of fuels, including methane, ethanol, and fuel oils (Demirbas, 2010). Many of these have been proposed to be routed to more complex chemicals through reforming processes (Bhujade et al., 2017).

Valorization of Co-Products

In order to compete with fossil fuels, biofuels must provide attractive economics. This can be achieved by increasing the cost of petroleum products through pricing nonrenewable carbon (or other mechanisms), or the value of algae cultivation can be further increased by production of additional products. Biomass conversion to biofuels inherently creates waste products from unused biomass, primarily composed of protein and carbohydrates. These can be consumed by anaerobic digestion to produce biogas, a low-value end product. Or, they can be converted into a variety of more valuable products. Combined approaches that utilize photosynthetic, fermentative, and chemical methods can be employed to produce products with high value. For instance, a combined algal processing method capable of producing multiple products from algae biomass was recently demonstrated (Miara et al., 2014). In such systems, algal carbohydrates can be diverted to fermentative production of ethanol or other commodity chemicals, such as succinic acid (Raab et al., 2010) from metabolically engineered yeast, while the proteins may be applied to adhesive manufacturing (Roy et al., 2014). Examples of co-products that may be valorized to improve the economics of biofuel production from algae include dietary protein, polyunsaturated fatty acids, and pigments.

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Dietary protein. Algae have long been viewed as an attractive source of dietary protein, both as animal feeds and for human consumption (Becker, 2007). Green algae contain between 40 and 70 percent of their dry weight as protein, and the amino acid profile of most algae compares favorably with common food proteins. A few studies have been performed to determine algae's protein efficiency ratio (PER), which reflects an animal's weight gain per unit of protein consumed; one study found algae offered up to 80 percent PER compared to milk proteins (Becker, 2004) while incurring a substantially smaller footprint than milk production in terms of freshwater resources and arable land (Bleakley and Hayes, 2017). Protein productivity from algae has been estimated at up to 50 times that of soybeans per acre of land. This suggests green algae has the potential to supplement or replace crops for animal feed with vastly reduced demands for arable land, but studies have not been validated at scale.

Polyunsaturated fatty acids. Many green algae naturally produce polyunsaturated fatty acids (PUFAs) that are valuable for humans and animals as food additives. While they are typically harvested from fish, PUFAs from algae represent a viable and more sustainable set of target molecules (Adarme-Vega et al., 2012). In particular the omega-3 varieties eicosapentaenoic acid and docosahexaenoic acid are valuable for the supplementation of many farmed animals, particularly carnivorous fish such as salmon and tuna (Ahmed et al., 2012; Bimbo, 2007). Omega-3 feeding studies have also been performed on cattle and poultry (Nitsan et al., 1999; Ponnampalam et al., 2006). In addition, omega-3 fatty acids demonstrate a consumer market as neutraceutical products that is currently dominated by fish oils.

Pigments. Colorants are manufactured as additives to foods, drinks, cosmetics, and a host of other products in order to increase the appeal of the product to the consumer. Some pigments are manufactured utilizing fossil fuel sources such as coal. Algae are well known for their ability to produce a variety of pigments and could provide a more sustainable alternative to the utilization of fossil fuels (Kaur et al., 2009). One well-known example of the successful application of algae for the commercial production of pigments is astaxanthin (see Box 5-1). The manufacture of other pigments with algae remains a potential opportunity for further exploration.

Box 5-1

Astaxanthin

Astaxanthin is a carotenoid pigment produced by a variety of microalgae. A polyunsaturated tetraterpenoid, astaxanthin presents a red coloration and is naturally responsible for pink or red pigmentation in fish, crustaceans, and shellfish through their diet. As a result, astaxanthin has become an important component in aquaculture feed to provide red/pink pigmentation to a variety of farmed seafood, particularly shrimp and salmon, with a market value approaching $250 million in 2010 (Borowitzka, 2013). It is also marketed as a nutraceutical, and a variety of vitamin supplements contain astaxanthin for its antioxidant properties. Cyanotech (Kona, Hawaii) produces astaxanthin from *Haematococcus pluvialis* in 25 hectares of open ponds, while Algatechnologies Ltd. (Ketura, Israel) uses photobioreactors with the same organism. BASF (Hutt Lagoon, Australia) produces the pigment from *Dunaliella salina* in 740 hectares of open ponds (Maeda et al., 2018). While commercial operations have shown profitability using open-air CO_2 absorption, CO_2 fixation by these commercial strains could benefit from increasing CO_2 concentration; up to a 5 percent level can provide significant improvements in biomass and astaxanthin levels (Chekanov et al., 2017).

Genetic Manipulation of Green Algae

The tools to facilitate genetic manipulation of green algae are far less advanced than tools for genetic manipulation of bacteria, yeast, and vascular plants. Key challenges include poor genome insertion, gene silencing, and unoptimized promoter systems. Nevertheless, some academic and industrial groups have attempted genetic modification of green algae for the purposes of improving photosynthetic efficiency, decreasing photodamage of the light harvesting complex, and optimizing the efficiency of carbon uptake and incorporation. Several products have also been sought from transgenic expression, including high-value therapeutic proteins, biohydrogen, lipids, and terpenoids (Gimpel, 2013).

Many species of green algae are genetically tractable, but *Chlamydomonas reinhardtii* has become the primary model system, with the majority of tools and techniques developed for this species (Rasala et al., 2013). Green algae have three separate genomes: nuclear, chloroplast, and mitochondrial. In *C. reinhardtii*, each of these genomes has been sequenced, and tools and protocols for genetic manipulation have been developed for each. Commonly, nuclear and chloroplast genomes have been primarily targeted for transgene expression, and each location involves special tools, advantages, and challenges. Engineering the nuclear genome for protein production offers benefits similar to other eukaryotic expression systems, including regulated expression, cytoplasmic protein folding machinery, access to posttranslational modification (such as glycosylation), and protein secretion. Furthermore, like many green algae, *C. reinhardtii* is a haploid organism. As a result, nuclear genome modifications can be used in combination with sexual breeding to provide additional genetic control. However, nuclear transformation currently suffers from several drawbacks, including random gene insertion, low protein expression, and gene

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silencing (Cerutti et al., 1997; De Wilde et al., 2000; Wu-Scharf, 2000). These complications are being actively researched, and some limited solutions have been recently developed. For instance, gene silencing has been addressed by directly coupling transgene expression with antibiotic resistance gene expression, therefore imparting a strict selection method for gene retention (Rasala, 2012, 2013). In addition, experiments employing new technologies for gene integration and knockout, including CRISPR methodologies, are currently under way (Ferenczi et al., 2017; Shin et al., 2016). Nevertheless, nuclear expression remains limited in terms of gene size, number, and complexity.

Tools and methodologies for manipulating gene expression in the chloroplast have achieved significant advances in recent years. Unlike nuclear expression, chloroplast expression allows homologous recombination, and multiple vectors, selection, and transformation methods have been developed. The green algae chloroplast offers an environment for protein expression, including chaperones and posttranslational modification enzymes that can facilitate proper protein and expression folding, and heterologous protein expression has achieved remarkable levels, sometimes as high as 10 percent of total soluble protein (Mayfield, 2007). Despite these benefits, chloroplast expression remains limited in terms of gene size and number, challenging the needs for engineering large operons and metabolic pathway design.

In the broader scheme of genetic engineering tools, photosynthetic organisms have historically received a low level of research support, and algae represent a small subset of this group (Gao et al., 2012). However, tools developed in recent decades underscore the potential for green algae as an ideal photosynthetic host organism. New and improved genetic tools for green algae genetic manipulation remain a key need for the advancement of algae biomass applications. This includes development of genetic insertion (homologous recombination) technologies, identification of robust promoters for gene expression, development of synthetic operons for multiple gene incorporation, tools for engineering large genes and pathways, and novel selection methods.

Approaches Based on Cyanobacteria

Cyanobacteria are being engineered to directly convert solar energy, carbon dioxide, and water to biofuels and other products. Cyanobacteria-based approaches possess advantages over traditional biological production systems based on plants, green algae, or heterotrophic organisms. For example, cyanobacteria are more amenable to genetic manipulation than are algae and can therefore be adapted for the production of a wider range of products (Figure 5-1). The photosynthetic efficiency of cyanobacteria is two to four times higher than that of plants (Melis, 2009), and their cultivation does not compete with food crops for land usage. Cyanobacteria also do not have the sugar requirements of heterotrophic organisms such as *Escherichia coli* and yeast, although they have a reduced

growth rate and fewer available synthetic biology tools compared to these hosts. While heterotrophic hosts may be adapted to utilize cellulosic feedstocks these technologies are still not well developed and as such efficiency can be low. Cyanobacteria allow us to skip this carbon-harvesting step and fix CO_2.
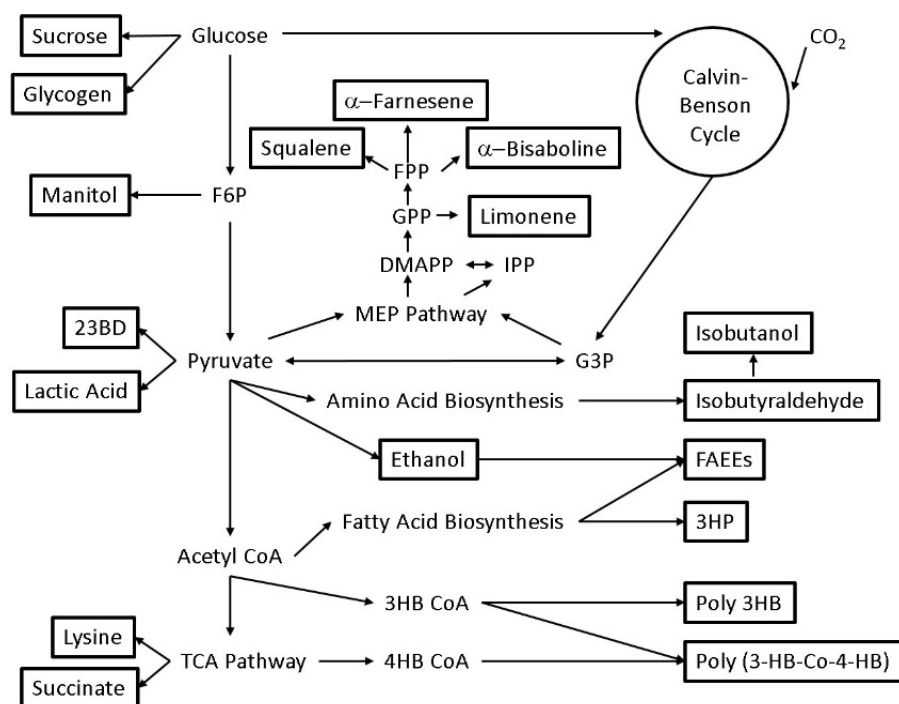
FIGURE 5-1 Example pathways for products from cyanobacteria. In the figure 23BD = 2,3-butanediol; FPP = farnesyl pyrophosphate; GPP = gross primary production; DMAPP = dimethylallyl diphosphate; IPP = isopentenyl diphosphate; 3HB CoA = 3-hydroxybutyryl-CoA; 4HB CoA = 4-hydroxybutyryl-CoA; FAEEs = fatty acid ethyl esters; 3HP = 3-hydroxypropionic acid; Poly 3HB = poly(3-hydroxybutyrate); and Poly (3-HB-Co-4-HB) = poly(3-hydroxybutyrate-co-4-hydroxybutyrate).[2]

There is a plethora of cyanobacterial species but only a few have been adapted to chemical production. The three predominant strains utilized for chemical production are *Synechococcus elongatus* PCC 7942 (7942), *Synechocystis* sp. PCC 6803 (6803), and *Synechococcus* sp. PCC 7002 (7002). These strains all have sequenced genomes, established culturing methods, and basic metabolic engineering tools (Berla et al., 2013; Markley et al., 2015; Nozzi et al., 2017; Yu et al., 2015), yet each strain presents its own unique advantages and challenges. 7942 is a freshwater unicellular cyanobacterium and studied for photosynthesis and genetic manipulation (Golden et al., 1987). 7002 is a marine

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[2] Reprinted from Carroll, Austin L., Anna E. Case, Angela Zhang, and Shota Atsumi. 2018. "Metabolic engineering tools in model cyanobacteria." Metabolic Engineering. doi:10.1016/j.ymben.2018.03.014 with permission from Elsevier

species capable of growth in a variety of conditions (salt, temperature, and light) (Batterton and Van Baalen, 1971), making it more apt to utilize natural saltwater resources. However, metabolic engineering has not been as well studied in 7002 as in freshwater species and synthetic biology capabilities for 7002 lag behind that of 7942 and 6803. 6803 has a good selection of genetic tools and can grow photomixotrophically.

Cyanobacteria have been engineered to produce a wide range of fuels, fuel precursors, and commodity chemicals. The productivities and titers (mostly on the order of milligrams per liter) are generally too low to make commercialization of the technology appealing, however, and these technologies have been demonstrated primarily on small, academic research scales. To move these technologies toward commercialization, it will be critical to reduce the cost of production and further advance tools for genetic manipulation and metabolic engineering of cyanobacteria.

Fuel Production

Fuels and fuel precursors that can be produced with cyanobacteria include ethanol, butanol, fatty acids, heptadecane, limonene, bisabolene.

Ethanol. Ethanol, a common biofuel candidate, has been produced in cyanobacteria by the transfer of two ethanol pathway genes from yeast. This production has been enhanced to form 5.5 g/L ethanol in *Synechocystis* sp. PCC 6803 (Dexter and Fu, 2009; Gao et al., 2012).

Butanol (n-butanol and isobutanol). Isobutanol has applications as a drop-in biofuel that could be integrated into current energy infrastructure. Production can be achieved by expressing heterologous 2-ketoisovalerate decarboxylase and aldehyde reductase that redirect carbon flux from the L-valine biosynthetic pathway to isobutanol resulting in a titer of 0.5 g/L in 7942 (Atsumi et al., 2009). n-butanol, which also has uses as a drop-in biofuel and is currently used in a variety of consumer products, can be produced in 7942 (Lan and Liao, 2011). The n-butanol biosynthetic pathway was constructed based on the natural n-butanol biosynthetic pathway found in *Clostridium acetobutylicum*. Examination and characterization of Coenzyme A-acylating (CoA) aldehyde dehydrogenases that are oxygen tolerant enabled production of butyraldehyde from butyryl-CoA. Final titers of 404 mg/L were achieved with productivity of 2 mg/L/h (Lan et al., 2013).

Fatty acids. Fatty acids can be used in the synthesis of biodiesels. Cyanobacteria natively produce free fatty acids in trace amounts. This production has been improved in 7942, 6803, and 7002. Free fatty acid overproduction leads to reduced cell fitness. Free fatty acid production in 7002 results in reduced negative impacts on the cell, and production can be

further improved by the nonnative expression of RuBisCO leading to >130 mg/L free fatty acids being produced (Ruffing, 2014). When coupled with native free fatty acid production, the expression of a heterologous diacylglycerol acyltransferase in tandem with an ethanol production pathway results in a variety of fatty acid ethyl esters (FAEEs) in 7942. This platform leads to the accumulation of up to 7 mg/L of FAEEs (Lee et al., 2017a).

Heptadecane. Long-chain hydrocarbons such as heptadecane (Table 5-1) can be readily used in fuel production for the synthesis of biodiesel. Heptadecane production can be achieved by capitalizing on the natural fatty acid production in the cell. Titers can be improved in strains that natively produce alkanes by overexpressing an acyl-ACP reductase/aldehyde-deformylating oxygenase (AAR/ADO) pathway. Expression of the AAR/ADO pathway from 7942 in a marine cyanobacterium results in up to 4.2 μg/g dry cell weight heptadecane (Yoshino et al., 2015).

Limonene. Limonene (Table 5-1) has applications as both a biofuel and a solvent. Limonene can be produced with the expression of a single heterologous gene for limonene synthase (LS) selected from spearmint for its high selectivity for limonene production. The expression of LS capitalizes on carbon flow through the native methyl-D-erythritol 4-phosphate (MEP) pathway, commonly found in plants, and funnel flow to limonene (Wang et al., 2016a). Establishing high LS expression is critical in improving titers. Limonene production has been established in 7942 and 7002 at 1 mg/L/OD_{730}/day (Wang et al., 2016a) and 4 mg/L (Davies et al., 2014) respectively. In 6803, carbon flux through the oxidative pentose phosphate (OPP) pathway is used to drive limonene production. Overexpression of two native enzymes (ribose-5-phosphate isomerase and ribulose 5-phosphate 3-epimerase) and expression of a heterologous geranyl diphosphate synthase gene establishes limonene production at 7 mg/L (Lin et al., 2017).

Bisabolene. Bisabolene (Table 5-1) has applications as a biodiesel candidate and production relies on carbon flow through the MEP pathway and the expression of a single heterologous gene, (E)-α-bisabolene synthase. Production has been established in 7002 resulting in 0.6 mg/L (Davies et al., 2014).

Commodity Chemicals Production

Commodity chemicals that can be produced with cyanobacteria include 2,3-butanediol, 1,3-propanediol, ethylene, glycogen, lactate, 3-hydroxypropanoic acid, 3-hydroxybutanoic acid, 4-hydroxybutanoic acid, isoprene, and farnesene.

2,3-Butanediol. 2,3-Butanediol (Table 5-1) is a commodity chemical used to make synthetic polymers (van Haveren et al., 2008) and can readily be converted to methyl ethyl ketone, a fuel additive and solvent (Tran and Chambers, 1987). 2,3-Butanediol relies on carbon syphoned from central metabolism in the form of pyruvate. The condensation of two pyruvate molecules, followed by decarboxylation and reduction through heterologously expressed genes, results in 2.4 g/L 2,3-butanediol after 21 days of production (Oliver et al., 2013). 2,3-Butanediol was similarly produced in 6803 (Savakis et al., 2013) and 7002 (Nozzi et al., 2017). In 7942 the addition of glucose and expression of *galP*, encoding a hexose symporter, allows growth using both CO_2 and glucose (McEwen et al., 2013). This modification permits continued 2,3-butanediol synthesis in both light and dark conditions, a potentially useful strategy for 24-hour metabolite production. Under photomixotrophic conditions 3 g/L 2,3-butanediol can be produced over 10 days (McEwen et al., 2016). Global metabolic rewiring of these strains for improved CO_2 fixation increases 2,3-butanediol titers, glucose utilization efficiency, and carbon fixation in both lighted and diurnal conditions (Kanno et al., 2017). Under continuous lighting, rewired 7942 produces 12.6 g/L 2,3-vutanediol (Kanno et al., 2017) when fed glucose and CO_2. Under natural 24-hour (diurnal) light cycling in the rewired strain, 5.7 g/L 2,3-butanediol is produced.

1,3-Propanediol. 1,3-Propanediol (Table 5-1) has a variety of uses including in polymers, paints, solvents, and antifreeze. Production in cyanobacteria is dependent on removal of carbon from the Calvin-Benson cycle in the form of dihydoxyacetone phosphate (DHAP). DHAP can be converted to 1,3-propanediol via a four-step heterologously expressed metabolic pathway. After the disruption of production bottlenecks 0.3 g/L 1,3-propandiol was produced in 7942 (Hirokawa et al., 2016).

Ethylene. Ethylene can be used to generate polyethylene, a widely used polymer, and in its gaseous state can be used to speed the ripening of produce. Production has been established in 6803 and relies on the expression of a single heterologous gene, *efe*, encoding ethylene forming enzyme (Efe). Efe converts 2-oxoglutarate from the tricarboxylic acid (TCA) cycle to ethylene. Partial deletion of *ntcA*, encoding the global transcription factor known for regulating carbon metabolism (Mo et al., 2017), exhibits a 23 percent increase in ethylene production and 1.5-fold increase in Efe activity in 6803 (Mo et al., 2017). Ethylene production in this strain reached 2.5 mL/h/OD_{730} (Mo et al., 2017).

Glycogen. Glycogen is a common form of energy storage and a potential carbon source for chemical production. It can also be converted into ethanol for use as a biofuel. 7002 naturally amasses glycogen under nitrogen-depleted conditions. Glycogen production can be improved by modifying culture conditions, including light intensity, CO_2 concentration,

and salinity (Aikawa et al., 2014). Improved production conditions result in 3.5 g/L glycogen after 7 days (Aikawa et al., 2014).

Lactate. Biological synthesis of lactic acid for biodegradable polymers has been established in 6803. Lactic acid production requires the heterologous expression of a single enzyme, lactate dehydrogenase, which pulls pyruvate from central metabolism to catalyze the conversion to lactic acid at a titer of 0.8 g/L after 2 weeks of cultivation (Angermayr et al., 2014). Further optimization of co-factor requirements leads to approximately 1.4 g/L lactate produced after 10 days in 7942 (Li et al., 2015).
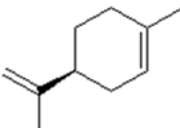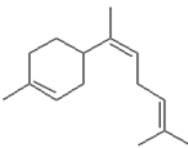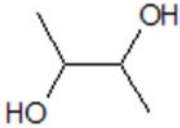
3-Hydroxypropionic acid, 3-hydroxybuterate, and 4-hydroxybuterate. 3-Hydroxypropionic acid (3-HP), 3-hydroxybuterate (3-HB), and 4-hydroxybuterate (4-HB) (Table 5-1) all have applications for the synthesis of polymers and plastics used in daily life. 3-HB was produced in 6803 and 7942 by the expression of a nonnative malonyl-CoA reductase, which converts malonyl-CoA to 3-HP. Malonyl-CoA natively feeds into fatty acid biosynthesis. This production can be aided by streamlining carbon flux to malonyl-CoA, expressing malonyl-CoA reductase, and optimizing nicotinamide adenine dinucleotide phophaste (NADPH) levels, resulting in 0.8 g/L after 6 days (Wang et al., 2016b). 7002 has been demonstrated to produce poly-3-hydroxybutyrate and poly-3-hydroxybutyrate-co-4-hydroxybutyrate through the introduction of a gene cluster from *Chlorogloea fritschii* PCC 9212 (Zhang et al., 2015). 3-HB production relies on native acetyl-CoA production, which can be converted to 3-HB in two consecutive steps. Alternatively, 4-HB can be produced by pulling carbon from the TCA cycle in the form of succinic semialdehyde. 3-HB can be produced by itself or in combination with 4-HB to create a copolymer. Production can reach 0.05 g/L of 3-HB or 4.5 percent total cell dry weight of the copolymer, with 4-HB accounting for 12 percent of the copolymer (Zhang et al., 2015).
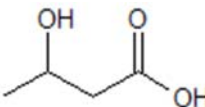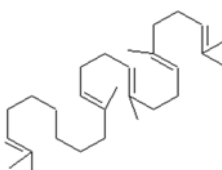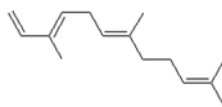
Isoprene. Isoprene is commonly used for the production of synthetic rubbers. Overexpression of the native MEP pathway and the expression of plant isoprene synthase gene (*ispS*) in 7942 results in the production of isoprene. With this production platform 1.3 g/L isoprene was produced after 21 days (Gao et al., 2016).

Squalene. Squalene (Table 5-1) is widely used in the food, personal care, and medical industries but its commercial production is unreliable and nonideal. Squalene production has been previously established in heterotrophic hosts, such as yeast. Similarly, squalene was produced in 7942 by the overexpression of the native MEP pathway in addition to the expression of a heterologous squalene synthase from yeast (Choi et al., 2017). Following optimization in carbon flux, the expression of this pathway results in 50 mg/L squalene.

Farnesene. Farnesene (Table 5-1) has been used as a precursor for high-performance polymers and as a jet fuel candidate. Production in 7942 was achieved by the heterologous expression of a single gene encoding farnesyl synthase, which funnels carbon out of the MEP pathway in the form of farnesyl diphosphate. The engineered strain produced 5 mg/L of α-farnesene (Lee et al., 2017b).

TABLE 5-1 Summary of commodity chemicals and fuels that are currently synthesized from CO_2 from cyanobacteria and their reported production.

Compound	Strain	Reported Production
Ethanol	*Synechocystis* sp. PCC 6803	5.5 g/L
Isobutanol	*Synechococcus elongatus* PCC 7942	0.5 g/L
n-Butanol	*Clostridium acetobutylicum*	2 mg/L/h
Fatty acids	*Synechococcus elongatus* PCC 7942 *Synechocystis* sp. PCC 6803 *Synechococcus* sp. PCC 7002	>130 mg/L
Heptadecane	*Synechococcus elongatus* PCC 7942	4.2 μg/g dry cell weight
Limonene	*Synechococcus elongatus* PCC 7942 *Synechococcus* sp. PCC 7002 *Synechocystis* sp. PCC 6803	1 mg/L/OD730/day 4 mg/L 7 mg/L
Bisabolene	*Synechococcus* sp. PCC 7002	0.6 mg/L
2,3-Butanediol	*Synechococcus elongatus* PCC 7942	2.4 g/L (after 21 days) 3 g/L (after 10 days, photomixotrophic conditions) 12.6 g/L (continuous lighting with glucose and CO_2) 5.7 g/L (23-hour light cycling)

Compound	Strain	Reported Production
1,3-Propanediol	*Synechococcus elongatus* PCC 7942	0.3 g/L
Ethylene	*Synechocystis* sp. PCC 6803	2.5 mL/h/OD$_{730}$
Glycogen	*Synechococcus* sp. PCC 7002	3.5 g/L (after 7 days)
Lactate	*Synechocystis* sp. PCC 6803 *Synechococcus elongatus* PCC 7942	0.8 g/L (after 2 weeks) 1.4 g/L (after 10 days)
3-HB	*Synechococcus elongatus* PCC 7942 *Synechocystis* sp. PCC 6803	0.8 g/L (after 6 days)
Isoprene	*Synechococcus elongatus* PCC 7942	1.3 g/L (after 21 days)
Squalene	*Synechococcus elongatus* PCC 7942	50 mg/L
Farnesene	*Synechococcus elongatus* PCC 7942	5 mg/L

Genetic Manipulation of Cyanobacteria

While some target fuels and chemicals can be produced through exploitation of naturally occurring cyanobacteria traits, manipulation of organisms' genetic material can enable production of many other target molecules. An understanding of areas where desired genetic material may be inserted without interrupting essential functions (gene integration and plasmids), ways to control production of the desired chemical target (promoters and riboswitches), and ways to tell the cell where to start and stop generating the target

molecule (ribosomal binding sites) are necessary in order to conduct genetic manipulations. CRISPR is another tool for reliable insertion of desired genetic material into host cells.

In addition to an enhanced ability to introduce and control novel pathways in cyanobacteria, a thorough understanding of the flow of carbon through the cell's metabolism is key to creating an industrially relevant production system. Techniques for improving carbon flux have included the use of carbon sinks, disrupting side pathways, removing inhibitors, and protein fusions to improve rate. While these techniques have pushed cyanobacteria toward industrial relevance there is still much that is unknown and needs further study.

Metabolic Engineering of Cyanobacteria

One of the primary challenges of chemical production in cyanobacteria is the low titers that result from most pathways. Production is usually limited to the milligram per liter (mg/L) order. A great deal of effort has gone into engineering RuBisCO, the primary carbon capture mechanism in cyanobacteria. While some improvements have been made (Whitney et al., 2011), RuBisCO has proven very difficult to improve, and alterations still remain below the required threshold for wide-scale chemical production.

An alternative to RuBisCO engineering is the supplementation of cyanobacteria with alternate carbon sources including glucose, glycogen, acetate, and xylose. While these carbon sources effectively improve titers, this additional carbon is not always directed toward chemical production and is often lost as biomass. Careful rewiring of carbon integration into metabolism can help improve this carbon utilization and act as a carbon sink to improve CO_2 fixation (Oliver and Atsumi, 2015; van der Woude et al., 2014). However, this approach requires a detailed understanding of carbon metabolism in the cell and how an alternate carbon source is being incorporated. In addition, these alternate carbon sources can increase the risk of contamination. As a slow-growing organism, cyanobacteria in culture can quickly become overcome by competing organisms that can utilize sources such as glucose. The necessity of using stricter techniques to prevent contamination, combined with the added cost of the alternate carbon source, can significantly raise production costs and eliminate some of the advantages of using cyanobacteria as a host strain.

In order to optimize carbon flow, researchers must fully understand it. Genome-scale models (GSMs) are important tools for assessing and engineering metabolic systems. The models may be used to describe an organism's entire metabolism utilizing genomic information (Broddrick et al., 2016; Kim et al., 2017; Shirai et al., 2016; Triana et al., 2014). It would be challenging to optimize production of a target chemical, identify bottlenecks, and target the best production system for the host without GSM. GSM-directed engineering has been successfully used to improve a variety of production platforms in *E.*

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coli, including 1,4-butanediol (Yim et al., 2011), lycopene (Alper et al., 2005), lactic acid (Fong et al., 2005), and succinate (Lee et al., 2005).

The transfer of GSMs from heterotrophs to photoautotrophs is a difficult process; one reason is that photosynthetic growth complicates simple factors, like energy input, making them complex and difficult to measure. The recent development of two GSMs (Broddrick et al., 2016; Triana et al., 2014) for 7942 allows for greater predictive power when making modifications to metabolism. New insights have been gained using a GSM developed for 7002 (Vu et al., 2013), which could help engineer the strain (Hendry et al., 2016). Based on this model it has been predicted that up to 10 percent of fixed carbon could be rerouted to production (Vu et al., 2013). These predictions have not been confirmed experimentally.

Construction of a comprehensive GSM for 6803 has attempted to resolve many of the problems that are seen in 7942 and 7002 with GSM development in cyanobacteria (Hucka et al., 2003; Knoop et al., 2010; Stanford et al., 2015). However, automated assembly of key GSM components is prevented by incongruent gene annotations and database nomenclature. GSM analysis uses 3,167 genes to study gene function, carbon metabolism, photosynthesis, and chemical production (Shirai et al., 2016; Yoshikawa et al., 2017). These models can identify deletions of native metabolic reactions that compete for reductive power required in targeted chemical production successfully (Yoshikawa et al., 2017). While traditional GSMs are limited to the native genes found in 6803, recent iterations incorporate nonnative metabolic reactions to construct hybrid phototrophic and heterotrophic cyanobacteria models (Saha et al., 2016; Shirai et al., 2016). These expanded models can predict new strategies for metabolic pathway construction and increase yields in targeted chemical production.

Synthetic biology tools are essential to utilize a strain as a production host. These tools can range from sites for the expression of nonnative genes to systems for controlling gene expression or tools for genetic manipulation (Albers et al., 2015; Immethun et al., 2017; Ueno et al., 2017). Heterotrophic hosts such as yeast and *E. coli* have well-developed synthetic biology toolboxes; however, these tools are often incompatible with photoautotrophic hosts such as cyanobacteria. In fact, tools developed for cyanobacteria are often difficult to transfer between strains, necessitating the development of a unique set of tools for gene integration and controlling gene expression on a transcriptional and translational level for each strain. Many of these tools have been developed for cyanobacteria (Berla et al., 2013; Golden et al., 1987; Markley et al., 2015). In addition to the difficulty of transferring tools between hosts, it can also be difficult to transfer pathways between host organisms. Gene expression, intermediates, and final products have varying toxicity across strains. Each strain can have a unique codon preference, altered enzyme activities, and constitutive promoters. One of the greatest challenges to metabolic engineering efforts for cyanobacteria is the careful tailoring of tools to each strain.

Key Considerations for Photosynthetic Approaches

Whether they involve the cultivation of green algae or cyanobacteria, photosynthetic approaches to carbon dioxide utilization raise a unique set of considerations relevant to their costs, benefits, environmental impacts, and social acceptability. Key considerations include the impact of the cultivation method used, restrictions in the use of genetically modified organisms, the degree of CO_2 solvation, nutrient requirements and downstream burdens, impacts on water and land use, and availability and suitability of CO_2 waste streams.

Impact of Cultivation Method

A key consideration for algae biomass production is the selection of cultivation method. Both open ponds and closed photobioreactor (PBR) designs have been implemented on academic and industrial scales (Figure 5-2). Open pond designs commonly employ oblong, "raceway" designs (Benemann et al., 1978) in which a high rate of water movement can be achieved with paddlewheels or air lift pumps. Raceway ponds have proven to be the dominant design, and their design has changed little in three decades, as their construction is believed to be among the least expensive of reactor designs. Raceway ponds can vary in size from several square feet to a hectare or more, and typically employ polymer bed liners and paddlewheel-style impellers. Bed liners are a requirement in some jurisdictions to meet water treatment codes, and the use of any genetically modified species may also mandate such barriers. The cost of bed liners commonly dominates the capital costs of a raceway pond, particularly with increasing size (Rogers et al., 2014).

FIGURE 5-2 Examples of algal cultivation technologies: (a)[3] and (b)[4] are different types of closed photobioreactors and (c)[5] an example of an open raceway pond.

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[3] Photo by IGV Biotech.
[4] Huang et al., 2017.
[5] https://www.energy.gov/eere/bioenergy/production (accessed October 10, 2018).

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Closed PBRs can involve a variety of scales, materials, and designs (Gupta et al., 2015)**,** many of which serve to optimize solar radiation upon the biomass culture. The simplest and most common PBR implements a "hanging bag" approach, where polyethylene tubes are suspended vertically with air and CO_2 diffusers to provide agitation and carbon addition (Martínez-Jerónimo and Espinosa-Chávez, 1994). Multiple larger system designs have been introduced in recent years using a variety of materials. Inherent in the viability of any PBR system is temperature control, a common challenge of closed systems, and the ability to agitate the culture, typically with pumped liquids.

The capital and operational costs of PBRs are considerably higher than those for open ponds, and the adoption of each technology is dependent on multiple factors (Richardson et al., 2012). Closed PBRs have the benefit of tight control over cultivation conditions, including temperature, CO_2 and O_2 levels, sun exposure, contaminants, and evaporation. As a result, culture density can reach levels not obtainable in open ponds (Schoepp et al., 2014). The ability to exclude contaminants and exogenous species, including predators, offers additional benefits. As a result, closed PBRs have been favored for the production of high-value products, where product purity is favored over low-cost cultivation. Similarly, open ponds have been favored for the production of biofuels given the need to minimize production costs.

Use of Genetically Modified Organisms

Current U.S. law and regulations tightly constrain the use of genetically modified algae in outdoor open ponds due to concerns regarding containment and spread of genetically modified organisms (GMOs). A limited study was recently performed to evaluate the dispersal, colonization, and impact of GMO algae into native water bodies (Szyjka et al., 2017). The particular study found that while broad dispersal occurs, impact on indigenous species was viewed as negligible. Additional work in this area is needed.

Degree of CO_2 Solvation

A major challenge to waste CO_2 utilization in all aquatic systems is CO_2 solvation. Simple sparging of gases in aqueous solutions results in costly and inefficient solubilization. Two methods have been developed: one utiliizes an amine-based CO_2 concentrator, followed by thermal stripping, and the second uses carbonate salts to deprotonate solvated CO_2 into soluble bicarbonate. The latter method has also been shown to be improved with the use of exogenous carbonic anhydrase, an enzyme that catalyzes CO_2 solvation (Hernandez-Mireles et al., 2014). Each of these methods contains drawbacks, such as thermal input or high pH values. While some strains of algae can adapt

to these conditions, more research is required to improve their integration into large-scale biomass cultivation (Könst et al., 2017). Some algal strains produce extracellular carbonic anhydrase to facilitate CO_2 solvation (Huertas et al., 2000).

Nutrient Requirements and Downstream Burdens

As with all photosynthetic crops, cultivating algae requires the application of fertilizers such as phosphorus and nitrogen. This has raised concerns that algae cultivation could contribute to eutrophication (excessive algal growth due to the influx of nutrients) in freshwater and coastal zones. Eutrophication is already a serious environmental concern in many areas due to agricultural runoff and municipal wastewater. To prevent algae cultivation from further compounding this problem and even partially address eutrophication, some have advocated the use of municipal and agricultural wastewater as sources of nutrients for algal cultivation (Woertz et al., 2009), thus capturing these nutrients with biomass cultivation before they reach downstream water bodies (Abdel-Raouf et al., 2012; Benemann et al., 2003; Brune et al., 2003). These scenarios would require co-localization of algae cultivation and wastewater treatment, and model pilot studies show significant promise (Bohutskyi et al., 2016; Chekroun et al., 2014). Nutrient recycling is also an important area of research for algal cultivation both as a means to minimize waste and as part of efforts to conserve water use (Rösch et al., 2012).

Impacts on Water and Land Use

Algae biomass cultivation depends upon plentiful sources of water. This poses concerns related to competition for scarce freshwater resources. However, algae are naturally abundant in a variety of environmental conditions, including freshwater, saltwater, brackish water, and a number of extreme environments. Both freshwater and saltwater algal strains have been used for demonstration and pilot-scale programs. Saline groundwater can be sourced throughout the United States. Other viable sources are ocean water and municipal wastewater (Farooq et al., 2015). As a result, freshwater resources need not be threatened by algae cultivation. The recycling, treatment, and disposal of water used for algal biomass has also been a topic of research interest because the life-cycle implications of the type of water used and whether it is recycled are significant (Guieysse et al., 2013; Yang et al., 2011).

Land use is also an important consideration, given that converting CO_2 waste from a single power plant would require dozens of hectares of biomass cultivation. Since algae cultivation does not require arable land, it will not compete with agriculture and can valorize regions with marginal or saline soils. Like traditional agriculture, the species

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selection will depend upon local climate. Endemic algae species have been studied for a variety of climates and environmental conditions.

Availability and Suitability of CO$_2$ Waste Streams

To achieve maximal biomass production, CO$_2$ must be supplied to algae cultivation. For many pilot-scale installations, sourcing CO$_2$ has presented a challenge that has been overcome through on-site compressed CO$_2$ storage and delivery. Economic studies have indicated that co-localization of power generation with biomass production can provide significant advantages (Kadam, 1997; Zeiler et al., 1995). Common CO$_2$ concentrations of flue gas from power generation ranges from 12 to 15 mol%, and these concentrations can be efficiently assimilated by algae biomass. Several pilot-scale facilities have implemented this strategy, whereby flue gas is utilized at the site to provide CO$_2$ to algal cultures (Chen et al., 2012; de Morais and Costa, 2007; Wang et al., 2008). Such co-localization strategies dominate technoeconomic analyses, as transportation of CO$_2$ through pipelines or vehicles would require purification and concentration of CO$_2$ from the source and fail to take advantage of the inherent flexibility of photosynthetic microorganisms to utilize a range of CO$_2$ concentrations.

Biomass utilization of CO$_2$ from industrial power plants provides the potential opportunity for large-scale carbon capture. Natural gas–fired power plants offer a waste stream with low sulfur and nitrogen content. The low levels of NO$_x$ and SO$_x$ present in the waste stream ultimately can be metabolized by most strains of algae and, as such, require considerations primarily for transport, heat exchange, and time of use (Radmann et al., 2011). Coal-fired power plants, on the other hand, present the challenge of additional contaminants. If not adequately purified, these waste streams can include contaminants known to be algecidic such as arsenic, cadmium, mercury, and selenium (Vocke et al., 1980). In addition to posing challenges for biomass cultivation, trace metals and other contaminants that derive from flue gas may limit potential applications   of biomass products. For example, products derived from coal-fired flue gas are likely to contain more contaminants, making these sources better suited for biofuel applications than for the production of protein for animal feed.

NONPHOTOSYNTHETIC APPROACHES TO CARBON UTILIZATION

Commercializing microbial production has always been an economic challenge due to the high cost of carbon feedstocks and low product yields. While significant work has been done to increase yields in recent years, the need to feed cultures with high-cost sugars is still an issue. Photosynthetic organisms like algae and cyanobacteria mitigate this

problem by utilizing CO_2 as their feedstocks, but they are slow growing and it is difficult to achieve industrially relevant productivity and scale up the production systems. Nonphotosynthetic organisms that can convert gases like CO_2 or methane have become prime targets for microbial production due to their wide diversity of pathways and growth rates. A summary of nonphotosynthetic approaches is shown in Table 5-2.

TABLE 5-2 Summary of nonphotosynthetic approaches to carbon utilization products.

Product	Route
Acetogens	Carbon dioxide fixation Two-state integrated process Carbon monoxide fixation
Acetate	Direct electron transfer from electrodes to microorganisms
Succinate	Direct electron transfer from electrodes to microorganisms
Alcohols	Indirect electron transfer via electrochemically synthesized electron donors
Pyruvate	Indirect electron transfer via electrochemically synthesized electron donors

Nonphotosynthetic biological systems possess a number of potential advantages over photosynthetic systems. These include a wide variety of organisms, a larger range of potential target chemicals, and the ability to avoid the inefficiency of photosynthesis. Aerobic systems also have the advantage of high productivity, capacity for continuous cultivation, and compatibility with artificial photosynthesis. Some nonphotosynthetic organisms can take advantage of low-cost, low-emissions electrons from renewable energy sources, and many can be cultivated with cheap and ubiquitous gaseous carbon feedstocks comprised of hydrogen, CO, and CO_2, such as industrial waste gas, biogas, or syngas.

There are also significant challenges that need to be addressed in order for technologies based on nonphotosynthetic organisms to reach maturity. These include many of the same challenges associated with photosynthetic systems, such as poor solvation of CO_2 and H_2, a lack of genetic tools and metabolic understanding, a limited number of strains that have been explored, and limited techniques for downstream processing of products. Nonphotosynthetic applications are at an earlier maturity level than

photosynthetic ones, and support is warranted on these applications to advance understanding and the maturity of these systems.

Approaches Based on Chemolithotrophs

Whereas cyanobacteria derive their energy and carbon from the reduction of CO_2, chemolithotrophs derive their energy from the oxidation of reduced inorganic compounds and their carbon from CO_2 (Kelly, 1981). This allows chemolithotrophs to perform light-independent CO_2 fixation, eliminating photosynthetic production issues like cell shading. However, cultivating chemolithotrophs is more complex as two inputs are required instead of one. Previous studies have characterized and tested the CO_2 fixation capabilities and commercial applications of selected chemolithotrophs (Schiel-Bengelsdorf and Durre, 2012).

Use of Acetogens with a Feedstock of CO2

Acetogens are a well-studied subset of mixotrophic chemolithotrophs that operate strictly under anaerobic conditions (Ragsdale and Pierce, 2008). One unique characteristic of these bacteria is the native Wood-Ljungdahl pathway (WLP), which fixes two CO_2 molecules into one acetyl-CoA with less energy than other carbon fixation pathways (Ragsdale, 2008). This gives acetogens an advantage as microbial production platforms because they can bypass carbon loss under certain fermentation conditions.

During traditional heterotrophic fermentation the conversion of sugar into acetyl-CoA results in one-third of all carbon lost to CO_2 production, limiting the maximum theoretical yield of products to 67 percent or less. During nonphotosynthetic mixotrophic fermentation the WLP reassimilates the CO_2 generated from sugar conversion, resulting in three acetyl-CoA and one adenosine triphosphate (ATP) for every molecule of glucose or hexose sugar. The amount of CO_2 reassimilated is dependent on the availability of NAD(P)H and, therefore, is inversely dependent on the target product's degree of reduction. If the product is highly reduced, less NAD(P)H is available for CO_2 fixation and vice versa.

Mixotrophic production has many advantages relevant to industrial viability. Using syngas in addition to sugar fermentation provides added reducing power for CO_2 reassimilation. Sugar catabolism, specifically glycolysis, provides ample ATP, which would otherwise be severely limited in WLP gas-only production. Mixotrophic production also potentially enables larger product yields by dividing carbon utilization between biomass and product formation.

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Carbon catabolite repression (CCR), in which one feedstock is preferred over the other (Bertsch and Muller, 2015), could present challenges for mixotrophic production. The concern with acetogens is that the sugar feedstock is preferred, thus reducing or eliminating the utilization of syngas for energy production or carbon fixation. However, nonphotosynthetic mixotrophic fermentation with syngas has been demonstrated in a variety of acetogenic microbes without CCR (Jones et al., 2016). In that study, carbon labeling fermentation resulted in *Clostridium ljungdahlii* with 73-80 percent and *C. autoethanogenum* with 51-58 percent of its acetate derived from syngas, demonstrating concurrent utilization of both feedstocks with little CO_2 lost from glycolysis. The study was also able to engineer *Clostridium ljungdahlii* to produce acetone, a commodity with a market of $8 billion.[6] Acetone anabolism does not require additional NAD(P)H downstream of acetyl-CoA, allowing for greater CO_2 fixation. Mixotrophic production from a high-density continuous fermenter resulted in a titer of 10 g/L and a productivity of 2 g/L/h, 92 percent of the theoretical mixotrophic maximum compared to 138 percent of the theoretical heterotrophic maximum. However, metabolic engineering was not applied to the host strain, and reactor conditions were not extensively optimized, especially for scale-up. More research is necessary to overcome the low degree of reduction required for the target products. The capability to engineer acetogens is currently limited by knowledge gaps and insufficient engineering tools (Bertsch and Muller, 2015).

Use of Two-Stage Integrated Process

Given the limitations of engineering acetogens, a viable alternative is to use other well-studied organisms to produce the target chemicals using carbon provided by acetogen CO_2 fixation. In a demonstration of this approach, Hu et al. created a two-stage integrated process that converts syngas to hydrocarbons (Hu et al., 2016). In the first stage CO_2 and CO or H_2 are converted anaerobically to acetic acid by the acetogen *Moorella thermoacetica*. Acetic acid is then fed into the second stage where it is converted aerobically into lipids by *Yarrowia lipolytica*. Accounting for the fact that certain products are not readily formed under anaerobic conditions, this two-stage bioreactor process allows for the nonphotosynthetic fixation of CO_2 followed by acetate-dependent production of aerobic products. The fermentation conditions of *M. thermoacetica* and *Y. lipolytica* were optimized for acetate and lipid production, respectively. *M. thermoacetica* growth and production were divided into two phases. A CO-dependent growth phase was established under CO_2/CO conditions; then the reactor was switched to H_2/CO_2 to increase production of acetate. This allowed for a high cell density and high specific productivity, resulting in 0.9 g of acetate/L/h. Cell recycling was used in *Y. lipolytica* fermentation to decouple growth and lipogenesis from acetic acid consumption. This too allowed for a high cell

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[6] See https://www.hexaresearch.com/press-release/global-acetone-market.

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density and high lipid productivity. When combined into the two-stage reactor system the results were inferior to the individual reactors, producing 18 g/L of C16-C18 triacylglcerides from syngas with an overall productivity of 0.2 g/L/h and 36 percent lipid content. Despite this shortcoming, the CO_2 fixation rate exceeded the CO_2 generation rate, demonstrating the feasibility of a two-stage bioprocess to convert syngas into useful commodities.

Use of Acetogens with a Feedstock of CO

Some acetogens are able to efficiently convert CO into useable CO_2 via a carbon monoxide dehydrogenase. Of these acetogens, a few produce products other than acetate from acetyl-CoA, including ethanol, butanol, and butyrate (Kopke et al., 2011). Researchers have investigated the fermentation conditions required to boost ethanol production, such as by optimizing metal cofactor concentrations, pH, and trace nutrients, and sought to optimize bioreactor designs for peak gas-to-liquid volumetric transfer efficiencies (Daniell et al., 2012). This research has paved the way for the commercialization of acetogens in the production of various high-value commodities. For example, LanzaTech[TM], a company focused on converting fuel gases into useful commodities,[7] currently operates a 100,000 gallon per year commercial plant that utilizes steel flue gas for ethanol production. Their production scheme employs acetogens, such as *Clostridium autoethanegenum*, which can utilize CO_2 and H_2 or CO, with or without H_2.[8] Nonphotosynthetic fixation of carbon dioxide through gas fermentation in the presence of hydrogen is a scalable mechanism of nonphotosynthetic fixation of carbon dioxide. The company also has laboratory-scale pilots of butadiene, propylene, and 2,3-butanediol (being developed as a precursor to jet fuel).

Approaches Based on Bioelectrochemical Systems

Expansion of renewable energy has provided an avenue for the sustainable production of commodities through bioelectrochemical systems. Bioelectrochemical systems carry out artificial photosynthesis by providing microorganisms with electrons that the cells use to reduce CO_2 into small organic compounds. In a basic bioelectrochemical setup that draws electricity from a photovoltaic system, electrons are generated at the anode from water, an inexpensive source of electrons, or organic waste and sulfides, which increase the setup complexity but allow for electron recovery at lower potentials (Lovely

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[7] See http://www.lanzatech.com/.
[8] See http://www.lanzatech.com/wp-content/uploads/2014/05/LanzaTech_Ex_Summary_8.5x11_05_09_2014.pdf.

and Nevin, 2013). Microbes carry out the reduction of CO_2 into organic products at the cathode. This typically occurs under an anaerobic environment to prevent oxygen reduction from depleting available electrons and generating toxic by-products, such as H_2O_2.

Bioelectrochemical systems have the potential to be more productive than biological systems, especially photosynthesis-based systems. Currently, plant solar conversion efficiency of photonic energy caps at 3-4 percent at peak growth, whereas photosynthetic microbes grown in optimized bioreactors can reach 5-7 percent efficiency (Blankenship et al., 2011). By contrast, photovoltaic devices, which can utilize a greater extent of incident solar energy, have 14-18 percent efficiency. Coupling photovoltaic devices with biological CO_2 fixation can result in a more efficient production platform overall.

There are several methods of integrating electrocatalysis into microbial production; the differences between these methods lie in how the electrons are transferred into the biological system (Lovely, 2011). Early research focused on providing electron shuttles that would transfer electrons from the electrodes to electron carriers in the cell. The issue with this method is that the electron shuttles, such as neutral red, are expensive, add complexity to product recovery, and are unstable and toxic within the host organism. Current research is focused on two main approaches: directly transferring electrons from electrodes to microorganisms and indirectly transferring electrons via electron donors. It is unclear whether the direct or indirect approach will prove to be more scalable for commercialization; each method has inherent challenges that need to be overcome to become industrially viable. The integration of electrocatalysis and microbial production is a relatively new concept with research still in its infancy, and engineering bioreactors for electrocatalysis will be a substantial challenge.

Direct Electron Transfer from Electrodes to Microorganisms

The direct transfer of electrons from electrodes into microorganisms requires linking intercellular reductions with extracellular electrons. Electrotrophs typically transfer electrons out of the cell via conduit cytochromes and their accompanying transporters. To achieve bioelectrochemical production these cellular mechanisms need to be reversed to drive electrons into the cell. This reversion would allow electricity to push biosynthetic pathways toward producing high-value chemicals and fuels. Such approaches have been demonstrated in the production of succinate and acetate.

Succinate. Ross et al. (2011) investigated cathodic electron uptake via electrocatalysis experiments with the bacterial host *Shewanella oneidensis.* Since it is difficult to measure the transfer of electrons in cells, the experiments were performed under anaerobic conditions in which there was only one functioning fumarate reductase available, thus

making formate reduction electrode dependent. The electron transfer conduit in *S. oneidensis* is known as the multiheme *c*-type cytochromes (Mtr) respiratory pathway. To test the reversibility of the Mtr pathway and understand the role of its individual components, multiple gene deletions were made. The results indicated that reverse electron flux requires the outer membrane and periplasmic components of Mtr. Interestingly, the electrons needed to pass into the menaquinone pool in the cytoplasmic membrane before reentering the periplasm to reduce formate. While the study was able to demonstrate evidence for the reversibility of the Mtr pathway in *S. oneidensis*, it also underscored the substantial amount of research needed to investigate electron transport pathways before modifications can be made.

Acetate. Because the direct bioelectrochemical model does not utilize electron shuttles, the host is required to be in immediate contact with the electrode in order for outer membrane electron transfer proteins to interact with the electrode surface. This represents a critical challenge of this method as there are physical limitations to the amount of electrode surface area that can be made available. While some researchers (such as Ross et al.) have focused on elucidating the roles of electron transfer pathways, others have focused on improving efficiency through improved reactor designs and operations. For example, LaBelle and May sought to improve microbial electrosynthesis of acetate. Converting H_2 and CO_2 into acetate is advantageous as creating a single C–C bond is less challenging and acetate has substantial commercial applications as a feedstock (LaBelle and May, 2017). Previous research demonstrated that increased biomass leads to higher acetate production; in their study, LaBelle and May sought to implement that concept in acetogensis electrocatalysis by increasing biomass production at the cathode. They accomplished this by switching to a galvanic operation, which was able to provide a higher volumetric current density, thus providing more electrons and better access to the microbes. They also moved to a continuous flow reactor, which reduced nutrient limitations and alleviated product inhibition. These changes not only considerably increased the production and efficiency of acetate production but also decreased the operating costs. While production was boosted to 0.78 g/L/h, significantly more research is needed to further advance bioelectrochemical reactor systems, in particular to improve product recovery.

Indirect Electron Transfer via Electrochemically Synthesized Electron Donors

Electrons can be indirectly transferred from electrodes to microorganisms via electrochemically synthesized electron donors such as H_2, formate, ammonia, sulfide, or iron (Lovely and Nevin, 2013). The low redox potentials of H_2 and formate allow a favorable thermodynamic reduction of CO_2 into organic compounds. Ammonia, sulfide, and iron are less thermodynamically favorable because they have higher redox potential.

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They also require an electron acceptor, such as oxygen, which adds complexity to the electrocatalysis setup and makes these three electron donors less favorable. Of the two more favorable electron donors, formate is a prime target for bioelectrochemical production. H_2 has a low solubility, a low mass transfer rate in cells, and significant safety issues due to combustion concerns inside of pressurized reactors. Formate, by contrast, has high solubility and is readily converted into carbon and energy by cells. However, formate adds complexity to product recovery and can also accumulate and degrade at the anode, reducing yield. To be a viable electron donor, formate needs to be consumed at a rate equal to its production. Formate-facilitated electron transfer has been demonstrated in the production of alcohols and pyruvate.

Alcohols. Li et al. designed a bioelectrochemical production platform producing higher alcohols from CO_2-derived formate in *Ralstonia eutropha*, a lithoautotrophic bacterium (Li et al., 2012). They identified three major hurdles to overcome in their production scheme: (1) engineering *Ralstonia* to produce alcohols, (2) producing formate under culturing conditions, and (3) engineering *Ralstonia* to withstand electricity. Previously developed pathways for isobutanol and 3-methyl-1-butanol were successfully installed in *Ralstonia*. Using an In foil cathode and a Pt anode they were able to produce formate, but culture growth was inhibited. They identified O_2^- and NO as stress triggers and solved the issue by placing a ceramic cup around the anode, shielding the culture by quenching the reactive species. Fed solely on electricity and CO_2 the *Ralstonia* demonstrated healthy growth and a production of 140 mg/L mixed alcohols.

Pyruvate. In another demonstration, Tashiro et al. developed a CO_2 and formate fixation pathway in *E. coli* that converts two formate and one CO_2 into pyruvate (Tashiro et al., 2018). This pathway, named the reductive glycine pathway (RGP), is theoretically the most efficient route for formate assimilation. RGP has many advantages: (1) it is a linear pathway, (2) its reactions are thermodynamically favorable, and (3) there are no oxygen-sensitive pathways involved. The researchers tested various RGP modules against cellular growth in auxotrophs and confirmed their products via carbon labeling. They evaluated the electrochemical cultivation system with indium, tin, lead, carbon, and copper electrodes. Indium had the highest efficiency for formate formation and performed well during bacterial cultivation. Similar to *Ralstonia*, the formation of reactive oxygen species threatens *E. coli* growth and productivity, something that is solved by growing under anaerobic conditions. The RGP was successfully constructed in *E. coli*, but additional research is needed to continue strain modifications and link pyruvate, a central metabolite, to the production of chemicals and fuels.

A RESEARCH AGENDA FOR BIOLOGICAL UTILIZATION
OF CARBON DIOXIDE

While some methods for biological conversion of CO_2 into fuels and chemicals are well developed, others are in their infancy. All existing and emerging approaches have technical challenges and limitations, as well as barriers to commercial-scale implementation. Social acceptability and regulations also will play a role in the viability of these technologies. Stages of development and key barriers for various biological utilization approaches are summarized in Figure 5-3 and Table 5-3.
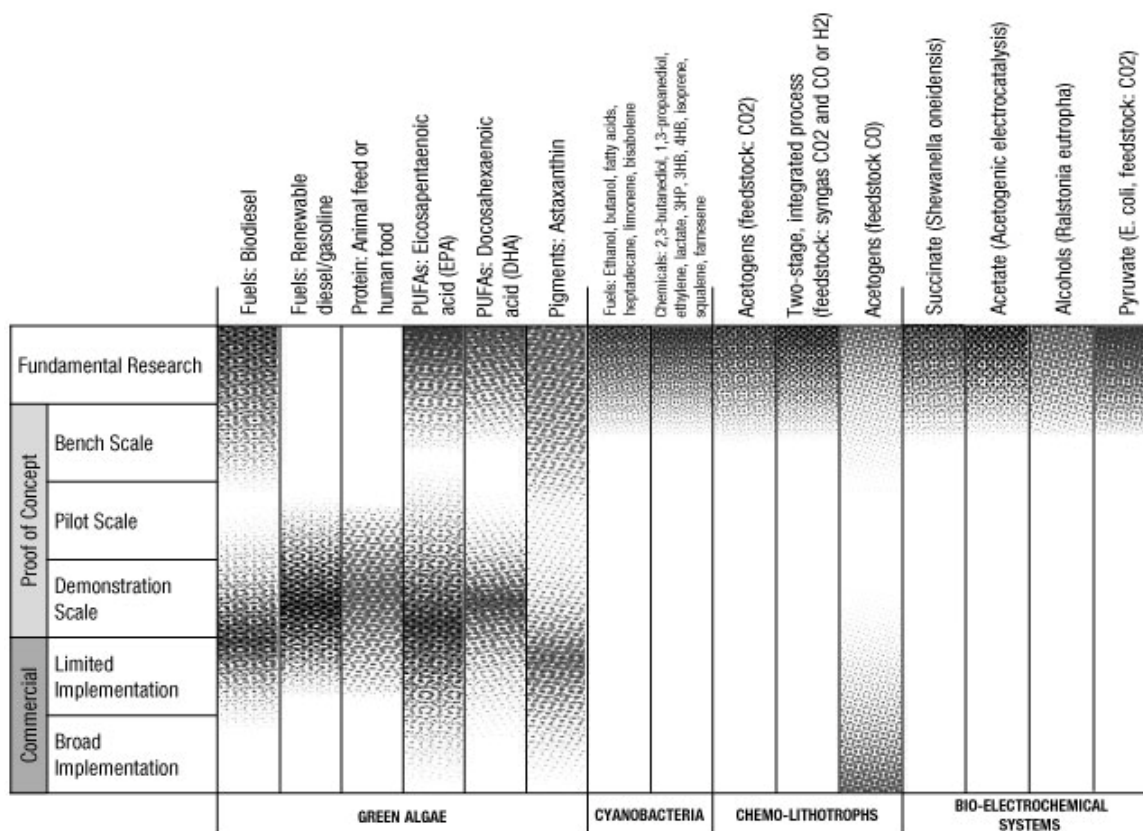
FIGURE 5-3 Stages of research activity for target products of carbon dioxide waste stream biological utilization. The higher density on the diagram indicates larger amounts of research activity in that stage. Blank areas indicate little or no research activity in that stage for a given product, indicating gaps in research activity.

NOTE: Fundamental research is defined as observation and reporting of fundamental principles of a scientific or engineering process, and formulation of a technology concept. The three proof-of-concept stages are defined as progressively larger-scale reactions to produce product. These include bench-scale processes where critical functions are proved and components or systems are validated in a laboratory environment and at a laboratory scale. Pilot plant scale is defined as a system validated in a relevant environment and at an engineering scale. Demonstration plant scale is defined as a full-scale system demonstrated in a relevant environment. Commercial-limited is defined as an actual system operating at a stage where product is being sold in the market in limited areas with specific advantageous geographical, regulatory, or other factors. Commercial-broad is defined as an actual system operating at a stage where product is sold in the market with opportunities not limited to specifically advantaged locations.

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TABLE 5-3 Key barriers for commercialization of the products from Figure 5-3.

Platform	Product	Key Barriers
Green Algae		Resource requirements (land, location, water)
	Fuels: Biodiesel	Hygroscopicity, cloud point, fouling
	Fuels: Renewable diesel/gasoline	Scalability and cost of hydrotreatment, renewable hydrogen
	Protein: Animal feed or human food	Scalability, social acceptance (particularly with regard to the use of waste gas)
	PUFAs: Eicosapentaenoic acid (EPA)	
	PUFAs: Docosahexaenoic acid (DHA)	Scalability, social acceptance
	Pigments: Astaxanthin	Limited market size
Cyanobacteria		Growth rate, smaller number of synthetic biology tools
	Fuels: Ethanol, butanol, fatty acids, heptadecane, limonene, bisabolene	Low productivity and titers, lack of genetic manipulation tools, scale-up
	Chemicals: 2,3-butanediol, 1,3-propanediol, ethylene, lactate, 3-HP, 3-HB, 4-HB, isoprene, squalene, farnesene	Low productivity and titers, lack of genetic manipulation tools, scale-up
Chemo-lithotrophs	Acetogens (feedstock: CO₂)	Low degree of reduction
	Two-stage, integrated process (feedstock: syngas CO₂ and CO or H₂)	Hydrogen requirement, low productivity and titers, scale-up
	Acetogens (feedstock CO)	Scalability
Bioelectro-chemical systems	Succinate (*Shewanella oneidensis*) Acetate (Acetogenic electrocatalysis)	Electrode surface, reactor design and operations improvements Product recovery, scalability
	Alcohols (*Ralstonia eutropha*)	Engineering organism to produce alcohols, produce formate under culturing conditions, and withstand electricity; scalability
	Pyruvate (*E. coli,* feedstock: CO₂)	Strain modifications, link to production of chemicals and fuels, scalability

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Priority Research Areas

Despite the barriers, there are numerous opportunities for advancing biological utilization of CO_2. Methods based on photosynthetic green algae are relatively mature; while they may be optimized to improve their cost competitiveness, there are opportunities, assuming the appropriate policy and social environment, to create valuable products. Cyanobacteria are a particularly promising platform for biological conversion because of their photosynthetic efficiency and genetic manipulability, but additional research is needed in order to improve titers and make cyanobacteria-based processes scalable and economically viable. Nonphotosynthetic biological carbon utilization systems avoid the use of high-cost carbohydrates and can be manipulated to create a wide variety of products. Compared to sugar cultivation, these cultures can be continuously cultivated for photosynthetic and nonphotosynthetic carbon dioxide fixation and methane conversion. Bioelectrochemical systems also hold promise because the electricity can help overcome the inherent inefficiency of photosynthesis. Priority research areas are described below.

Bioreactor and Cultivation Optimization

Research is needed to improve bioreactor system design for efficient carbon dioxide solvation, mass transfer, dewatering and harvesting, and management and recycling of water and nutrients. This may include development of better computational and modeling tools for optimizing cultivation processes. Advancement of nonphotosynthetic methods may require novel bioreactor design in order to incorporate new feedstocks or hybrid fermentative systems. This will improve culture monitoring technologies and facilitate scale-up of utilization.

Analytical and Monitoring Tools

Research is needed to improve culture monitoring technologies. This will facilitate scale-up.

Genome-Scale Modeling and Improvement of Metabolic Efficiency

Research is needed to develop and improve methods for in-depth computational modeling, genetic manipulation, biochemical validation, and fermentative demonstration. This will improve metabolic flux, including carbon dioxide uptake and incorporation, photosynthetic efficiency, metabolic streamlining, and product accumulation.

Bioprospecting

Research is needed to accelerate the identification and characterization of organisms or biological systems with unique attributes such as carbon dioxide uptake, various product profiles, photosynthetic efficiency, and environmental tolerance. This will enhance the ability to produce target products in diverse geographic locations.

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Valorization of Co-Products

Research is needed to develop feed and food uses for co-products of biological conversion, including studies in product safety and acceptability. This will improve the efficiency of energy and materials use and increase the economic value of biological conversion technologies.

Genetic Tools

Research is needed to enhance engineering of photosynthetic and nonphotosynthetic organisms, including expansion of tools for genetic incorporation, selectable markers, promoter elements, protein folding and stability, and posttranslational control. This will improve efficiency and rates of biomass production and selective product formation.

Pathways to New Products

Research is needed to identify biological pathways to produce nontraditional products and new products for unmet needs in commodity and specialty chemicals. This will expand the portfolio of products made via carbon utilization.

FINDINGS AND RECOMMENDATIONS

Finding 5-1 Biological conversion has a significant advantage over other technologies in that it does not require purified CO2 streams; however, co-localization with CO2 sources would be required due to barriers posed by transportation. Photosynthetic algal biomass production has some significant advantages compared with conventional crops in terms of its land footprint, water use footprint, and protein content. Photosynthesis is inherently inefficient though, requiring compensation with scale, making it land intensive.

Finding 5-2 When developing any type of photosynthesis-based system, it is important to consider the impact of the cultivation method, restrictions in the use of genetically modified organisms, the degree of CO2 solvation, nutrient requirements and downstream burdens, impacts on water and land use, and availability and suitability of CO2 waste streams.

Finding 5-3 Biofuels have potential to advance the circular carbon economy and reduce reliance on and environmental impacts of fossil resource extraction. Renewable fuel production has been limited in its implementation due to its high cost compared with fossil sources and the capital infrastructure necessary to catalytically hydrogenate lipid extracts.

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Finding 5-4 Algal protein has the potential to supplement or replace conventional crops as a source of animal and/or human food, but studies have not been validated at scale. Some carbon waste streams, such as those with heavy-metal contaminants, will be inappropriate for animal or human food applications.

Finding 5-5 Polyunsaturated fatty acids are a promising and potentially lucrative product of algal biomass. Pigments may be another valuable algae-based product. These applications may have the additional benefit of reducing pressure on conventional fish-based sources of these products.

Finding 5-6 Cyanobacteria possess many advantages over other biological systems because they can easily be manipulated genetically to create different products, they are more efficient photosynthetically, and they can use CO_2 directly. Challenges with cyanobacteria include slow growth rate and limited availability of synthetic biology tools.

Finding 5-7 Nonphotosynthetic microbial systems that can use CO_2 rather than sugars hold promise for utilization of gaseous carbon waste feedstocks. Of particular interest may be mixotrophic acetogens.

Recommendation 5-1 Researchers should improve bioreactor system design for efficient carbon dioxide solvation, mass transfer, dewatering and harvesting, and management and recycling of water and nutrients.

Recommendation 5-2 Researchers should improve culture monitoring technologies to facilitate scale-up.

Recommendation 5-3 Researchers should develop and improve methods for in-depth computational modeling, genetic manipulation, biochemical validation, and fermentative demonstration.

Recommendation 5-4 Researchers should enhance the ability to produce target products in diverse geographic locations by accelerating the identification and characterization of organisms or biological systems with unique attributes.

Recommendation 5-5 Researchers should develop feed and food uses for co-products of biological conversion.

Recommendation 5-6 Researchers should enhance engineering of photosynthetic and nonphotosynthetic organisms to improve efficiency and rates of biomass production and selective product formation.

Recommendation 5-7 Researchers should identify biological pathways to produce nontraditional products and new products for unmet needs in commodity and specialty chemicals.

Recommendation 5-8 Research into reducing the capital infrastructure of hydrotreatment of algal lipids or alternative pathways should be conducted by researchers in order to reduce the costs associated with biofuels. Sources of renewable hydrogen are also needed.

Recommendation 5-9 Research into large-scale biomass cultivation should be considered by researchers, given the potential for algal biomass to supplement or replace animal feed and possibly human food. The life-cycle implications of necessary high-purity contaminants present in carbon waste streams will need to be considered.

Recommendation 5-10 Research into nonphotosynthetic technologies should be considered by researchers, given the promising opportunities that are complementary to photosynthetic technologies.

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Methane and Biogas Waste Utilization

As described in Chapter 2, methane waste gas sources include emissions from oil and gas supply chains, which are primarily methane mixed with other low-molecular-weight hydrocarbons, and emissions from landfills, manure, sewage, and other waste management operations, which are primarily mixtures of carbon dioxide and methane (biogas). Biogas utilization has primarily focused on use of the methane content of the waste gas, so this chapter will treat biogas and methane utilization as a single topic. A few processes under development utilize both the carbon dioxide and methane content of biogas, and these will be noted as the technologies are described.

Methane utilization and utilization of methane derived from biogas fundamentally differ from carbon dioxide waste gas utilization. Carbon dioxide is a low-value, low-energy waste gas, which is often available in large quantity in single locations. Methane, in contrast, is a high-value, high-energy molecule. Because of its high value and high energy of combustion, methane recovered from waste gases is often used as a fuel and any other utilization pathways must compete against the fuel value of methane (NASEM, 2016). If utilization pathways are able to add more value to methane than its value as a fuel, then the extent of methane available to utilization processes could increase substantially. Methane is the principal constituent of natural gas, and more than 600 Tg/yr of natural gas is produced and used in the United States. Like carbon dioxide, chemical utilization pathways are both chemical and biological. Unlike carbon dioxide, methane does not have mineral carbonation use pathways.

COMMERCIAL TECHNOLOGIES FOR THE CHEMICAL UTILIZATION OF METHANE

A major commercial route for the chemical use of methane is steam reforming. Steam reforming of methane is the dominant route for the commercial production of hydrogen and is a mature technology which was viewed by the committee as outside the scope of this report. Another major commercial route for the chemical use of methane, considered outside the scope of this report, is the production of synthesis gas (syngas) through methane partial oxidation. In syngas production, methane is partially oxidized to form carbon monoxide, carbon dioxide, and water (see Eq 4-6). Through the water gas-shift reaction, the carbon dioxide and water can be transformed into molecular hydrogen and carbon dioxide, allowing the carbon monoxide to hydrogen ratio in the syngas to be controlled. Syngas has been used for decades as a feedstock for a variety of

commercial technologies. For example, in the Fischer-Tropsch process, which has been used commercially since the 1930s, syngas is converted to liquid hydrocarbon fuels.

In contrast to steam reforming of methane and partial oxidation of methane to produce syngas, which are mature commercial technologies, dry and tri-reforming of methane are still under active development. Dry reforming of methane (Eq 4) uses carbon dioxide as a feedstock rather than the water used in steam reforming (Eq 5), and generates synthesis gas (syngas) as a 1:1 mixture of CO and H_2. Although this is not the most useful ratio of CO to H_2 for conversion into chemicals, dry reforming is a useful strategy for converting two greenhouse gases into a valuable chemical feedstock and is a possible use for biogas waste streams that are mixtures of methane and carbon dioxide. In 2015 Linde built a pilot reactor for dry reforming, which uses a nickel or cobalt catalyst and also feeds in a small amount of water to increase the ratio of H_2 to CO. At this stage it is not clear if this technology or related systems which are in operation on a pilot scale in Japan will be commercially viable on a large scale. Dry reforming is challenging because it is highly endothermic. As a consequence it is typically performed at high temperature (> 800°C), which also reduces the thermodynamically favorable formation of coke. Noble metal catalysts show the best activity, while minimizing coke formation, but are expensive. Other options are to use noble metals to decorate nickel catalysts, to make nickel nanoparticles of a certain size, or to encapsulate the nickel catalyst, all of which significantly increase the activity of the base metal catalyst. Nevertheless, finding an economically viable catalyst that minimizes catalyst deactivation through the formation of coke remains the biggest challenge in dry reforming.

An alternative to the dry reforming of methane is tri-reforming.[2] In tri-reforming, three reactions occur in the same reactor: dry reforming (Eq 4); steam methane reforming (Eq 5); and partial oxidation of methane (Eq 6):

Dry reforming	$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$	(Eq 4)
Steam methane reforming	$CH_4 + H_2O \rightarrow CO + 3\ H_2$	(Eq 5)
Partial methane oxidation	$CH_4 + 0.5\ O_2 \rightarrow CO + 2\ H_2$	(Eq 6)
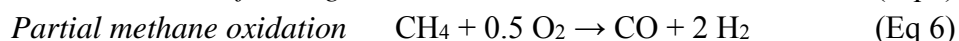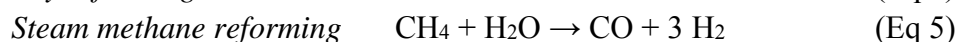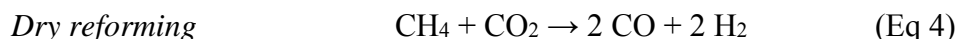
The net reaction involves the formation of an approximately two-to-one mixture of H_2 and CO from CH_4, CO_2, H_2O, and O_2. The steam reforming and dry reforming reactions are endothermic, while the partial oxidation is exothermic, which assists in providing the energy for the process. The reaction can be run at high conversions of CH_4 and CO_2 using nickel catalysts. The presence of H_2O and O_2 in the reaction mixture limits coke formation as a result of side oxidation reactions, but this is still a problem in catalysis. Current research is exploring the use of both supports and promoters to limit coking and this along with the design of nickel catalysts with specific shapes and sizes should be a focus of research. Additionally, improvements in the selectivity of tri-reforming are required to generate a commercially viable system.

DIRECT CHEMICAL UTILIZATION OF METHANE
WASTE GAS STREAMS

The direct conversion of methane into valuable products is a problem that has fascinated chemists for decades but has not resulted in the development of many industrial processes (Holmen, 2009; Karakaya and Kee, 2016; Schwach et al., 2017). Examples of commercial technologies include the conversion of methane and ammonia into hydrocyanic acid (Eq 7) (Andrussow, 1955), the production of acetylene through the partial oxidation of methane (Eq 8) (Pässler et al., 2000), and the formation of carbon disulfide via the reaction of methane with sulfur (Eq 9) (Folkins et al., 1950). The major challenge associated with methane conversion is selectivity. The C–H bonds in methane are very strong, whereas the C–H bonds in the potential products are typically weaker. Therefore, further reactions are more likely to occur with the product before all of the starting methane has been consumed. A summary of current research into the direct conversion of methane into more valuable chemicals is provided below, including an assessment of which areas of investigation should be prioritized.

$$2\ CH_4\ +\ 2\ NH_3\ +\ 3\ O_2\ \xrightarrow[-6\ H_2O]{Pt\ catalyst}\ 2\ HCN \qquad (Eq\ 7)$$

Hydrocyanic acid
1.3 million tons produced per year

$$CH_4\ +\ O_2\ \xrightarrow[\substack{-\ H_2,\ CO,\ CO_2,\\ \&\ other\ hydrocarbons}]{1500\ °C}\ C_2H_2 \qquad (Eq\ 8)$$

Acetylene
500 kilotons produced per year

$$2\ CH_4\ +\ S_8\ \xrightarrow[-4\ H_2S]{Si\ or\ Al\ catalyst}\ 2\ CS_2 \qquad (Eq\ 9)$$

Carbon disulfide
1 million tons produced per year
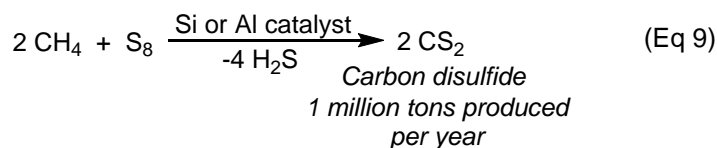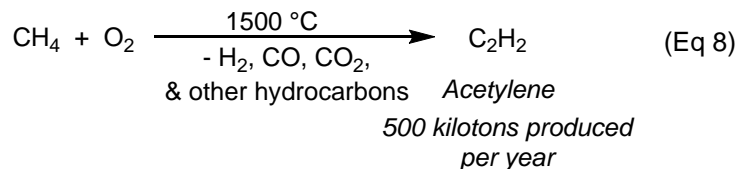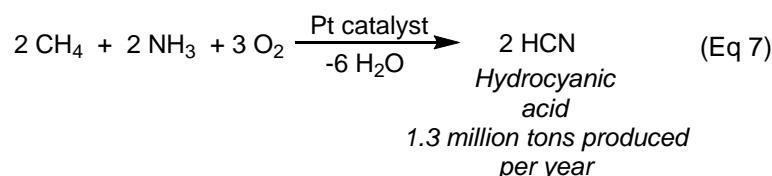
Methanol

The development of catalysts for the direct conversion of methane to methanol has been a high-profile target for the homogeneous, heterogeneous, and enzymatic catalysis community for more than 50 years (Gunsalus et al., 2017; Kondratenko et al., 2017; Ravi et al., 2017; Wang et al., 2017). Despite intense research an industrial process has remained elusive. The main difficulty in direct methane conversion is that the C–H bonds in methanol are weaker than the C–H bonds in methane and preferentially react under the relatively harsh conditions required to activate the strong C–H bonds in methane. Therefore, high yields of methanol can only be achieved at low

conversion. Both homogeneous and heterogenous reaction systems have been investigated. The major advantage of homogeneous systems compared to heterogeneous systems is that they can activate C–H bonds at low temperature (Gunsalus et al., 2017). However, they often require oxidants that are significantly stronger and less sustainable than O_2, which is the preferred oxidant. The best yields for homogeneous systems have been achieved in systems where methanol is protected in the reaction mixture as it is formed, so that it cannot undergo further reactions. For example, Perianna and co-workers oxidized methane in a concentrated solution of sulfuric acid using either a mercury- or platinum-based catalyst (Periana et al., 1993, 1998). The methanol that is formed is protected as methyl bisulfate, which is less reactive than methane. Similar strategies have used trifluoroacetic acid to protect the methanol in the form of a trifluoroacetate ester (Kao et al., 1991), but, like sulfuric acid, trifluoroacetic acid is highly corrosive, which makes it difficult to use industrially. An alternative strategy to prevent overoxidation of the methanol product is to use membranes to separate the product, but significant research into this approach is yet to be performed. At this stage the turnover frequencies, turnover numbers, and catalyst stability of the best homogeneous systems also need to be improved.

As a result of the potential ease in downstream product separation, heterogeneous catalysts have been even more widely studied than homogeneous systems for partial methane oxidation (Ravi et al., 2017). The most well-studied systems are based on molybdenum, iron, or copper. Molybdenum oxides have been studied for almost 50 years and especially when used in the form of multicomponent oxides give high selectivity to methanol due to product stabilization (Atroshchenko et al., 1965). Iron and copper systems have garnered attention as catalysts because these metals are present in the active site of different forms of the enzyme methane monooxygenase which catalyze the transformation of methane to methanol at room temperature (Figure 6-1) (Wang et al., 2017). Iron zeolites give high yields of methanol but typically use oxidants such as nitrous oxide or hydrogen peroxide, which have comparable expense to methanol. Copper zeolites give high yields of methanol using O_2 as the oxidant. The product of oxidation is normally trapped in the zeolite and water is co-fed into the system along with methane to release methanol as a product. This can either be done after methane has been fed through the reactor, which results in a chemical loop rather than true catalysis, or simultaneously. The key feature is that the trapping of the methanol in the zeolite protects it from further reaction in a similar way to trapping methanol with sulfuric acid in homogeneous systems. In general, it appears likely that, if an industrially viable system for methane conversion to methanol is to be developed, some kind of protection of the methanol product will be required to achieve high yields and conversion. This should be a focus of future research, along with fundamental catalyst design as large improvements in performance and stability are still required.
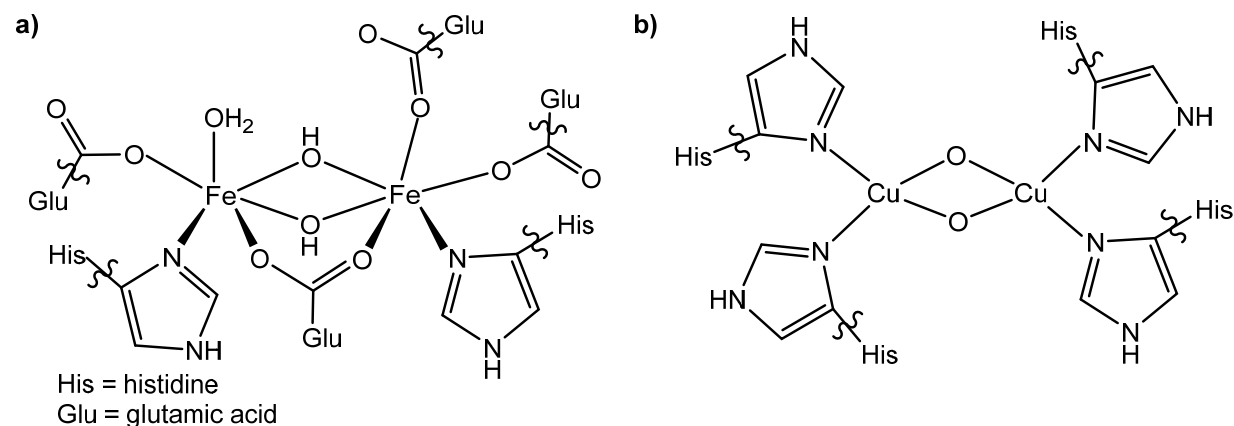
FIGURE 6-1 Active site structure of (a) iron and (b) copper containing methane monooxygenase.

Ethylene

Research into the oxidative coupling of methane to form ethylene started in the 1980s (Holmen, 2009; Karakaya and Kee, 2016; Schwach et al., 2017). In this process methane is coupled in the presence of O_2 to form ethylene and water, along with ethane and other higher-order hydrocarbons. At high temperatures (~700°C) a wide variety of different heterogeneous catalysts including systems based on Li/MgO, Fe_2O_3, and La_2O_3 can perform this reaction. At the moment this process generates significant quantities of ethane, C_3 products, CO, and CO_2 as well as ethylene. In particular, the formation of CO and CO_2 is problematic because it is difficult to separate these products from ethylene. Recently, several catalysts that can operate at lower temperatures (~500°C) have been developed and these systems offer advantages in terms of the energy input required, and preventing coke formation (Tang et al., 2014). Nevertheless, the major problems with current catalysts are the lack of selectivity to ethylene and catalyst stability. It has been estimated that approximately a 25 percent yield of ethylene is required in a single pass for the process to be commercially viable. Given the recent advances in the development of nanomaterials with well-defined morphology and preliminary results showing improved performance with catalysts of defined size and morphology, further research in this area is warranted.

In an alternative procedure to make ethylene, methane is heated in the absence of O_2 (Holmen, 2009; Karakaya and Kee, 2016; Schwach et al., 2017). In this case the other major products are ethane and H_2, but no oxygenates are formed. The ethane could be upgraded into higher-value ethylene using an oxidative dehydrogenation process. One of the major problems with this approach is that the reaction is thermodynamically unfavorable even at elevated temperatures (> 500°C) so the conversion of methane is low. Nevertheless, using a tantalum hydride catalyst supported on SiO_2, 98 percent selectivity to C_2 products can be achieved (at 0.05 percent conversion) (Tang et al., 2014). Another engineering problem associated with this reaction is that it is often run in two steps. First methane is exposed to the catalyst, which promotes the

formation of hydrogen-deficient CH_x fragments on the catalyst surface. Second, H_2 is introduced, which promotes C–C bond formation and cleans the surface of the catalyst. These steps need to be performed at different temperatures, which introduces a practical challenge. Further catalyst development is also required.

Aromatics

Benzene is an important precursor for a range of aromatic compounds including ethyl benzene, 1-methylethylbenzene, cyclohexane, and nitrobenzene. Approximately 43 million tons were produced in 2012. Typically, benzene is produced from the steam cracking or dehydrogenation of naphtha, or via the disproportionation or hydrodealkylation of toluene. An efficient synthesis of benzene from methane could provide advantages over these petroleum-based routes. In 1993, the methane dehydroaromatization reaction was discovered (Wang et al., 1993). In this process methane is converted into benzene and H_2. No oxygenates, including CO or CO_2, are generated in this process, which means that the H_2 is of suitable quality to be used directly in fuel cell applications. Unfortunately, the reaction is not thermodynamically favorable and at temperatures of around 900°C a benzene yield of approximately 12 percent is obtained, which is close to the thermodynamic yield (Tang et al., 2014). The formation of naphthalene is just as thermodynamically favorable as benzene, so it is typically observed as a by-product (Tang et al., 2014). The best catalysts are bifunctional zeolite-based systems, such as Mo-ZSM-5. The molybdenum sites are responsible for the methane activation and Brønsted acidic sites in the zeolite promote the aromatization reaction. A problem with the reaction is that a significant amount of coke is formed, which requires the catalyst to be regenerated using H_2. Future research should focus on strategies to remove benzene from the product stream to drive the reaction and increase the yield and on efficient methods to regenerate the deactivated catalysts from coking.

BIOLOGICAL APPROACHES FOR UTILIZATION OF METHANE WASTE GAS STREAMS

Various methanotroph species can utilize methane as their sole carbon and energy source (Kalyuzhnaya et al., 2015). Although methane conversion can occur under aerobic and anaerobic conditions, a subset of aerobic bacteria and gamma-proteobacteria are generally the focus of metabolic engineering efforts. This bacterial group converts methane into formaldehyde which is then processed by the cell in metabolic pathways commonly used in sugar catabolism, such as glycolysis. One such pathway converts formate into CO_2 which feeds into the Calvin-Bensen cycle to produce biomass. These sugar-catabolism pathways are utilized by common industrial strains, like *Escherichia coli* and *Saccharomyces cerevisiae*, that have been extensively investigated. This

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makes gamma-proteobacteria and similar methanotrophs more readily engineered to become a microbial production platform as more is known about the pathways.

To successfully implement methanotrophs as industrial hosts for methane conversion there are several fundamental issues that need to be addressed. The metabolic pathways downstream of methane assimilation are largely unknown or poorly understood, making metabolic engineering efforts challenging. This problem is compounded by a lack of knowledge of how carbon flux is driven and regulated in methanotrophs. Of key importance is the methane oxidation electron donors, including those involved in the first oxidative step converting methane to methanol via methane monooxygenase. For some of these issues genomic mining can be done to draw out comparisons and assumptions, but intensive experimental investigations are needed for confirmation.

In lieu of mapping methanotroph metabolism, the methane oxidation machinery could be installed into well-studied heterologous hosts, like *E. coli*. However, there has been no reported complete oxidative activity, with enzymes like the methane monooxygenase expressing poorly or with low activity (Balasubramanian et al., 2010; Jahng et al., 1996). This indicates significant research must be done before nonmethanotrophs can metabolize methane. One possible avenue would be high-throughput directed evolution followed by genetic screening. However, this method would most likely first require evolution to grow on methanol, then methane. Using methanotrophs for industrial production would also require extensive research, particularly into host selection, as some gamma-proteobacteria have faster growth rates while others are more readily engineered or have beneficial metabolic pathways. Whether the industrial strain will be native or heterologous, several strategies such as protein engineering are being carried out to improve the enzymes involved in methane biosynthesis.

Methane-based production faces considerable platform challenges, some common to microbial fermentation such as the risk of contamination, buildup of toxic intermediates, and the high cost of additives, like nucleic acids. Other issues are more specific, such as increased risk due to using a mixture of flammable gases, O_2 and CH_4. The low solubility of methane requires considerable process engineering efforts to provide large-scale microbial batches with enough carbon to grow and produce. This is especially important if the microbes are grown solely on methane, one of the factors that would make fermentation economically viable. Despite these challenges there has been a diverse group of methane-based chemicals produced, such as sugars, alcohols, amino acids, carotenoids, epoxides, and polymers (Kalyuzhnaya et al., 2015). Some of these have been tested by companies at commercial scales, although the commercialization of these products is still limited and metabolic engineering has not been implemented in many cases.

Calysta™ is a UK-based sustainable products company that has developed and commercialized FeedKind® protein, a high-nutrient-density product containing 71 percent protein and 9 percent fat. This alternative feed for fish, livestock, and pet nutritional products is composed of *Methylococcus capsulatus*, a naturally occurring methanotroph. In this case the host organism is the product, with its biomass content the commercial application. There are several

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environmental benefits of FeedKind, including no agricultural land use, utilizing 77-98 percent less water than agricultural products (Cumberlege et al., 2016).

In 2017 Calysta produced more than 5 tons of FeedKind and distributed commercial samples worldwide. They announced a collaboration with Cargill to build the world's largest gas fermentation facility on President's Island in Memphis, Tennessee. The 37-acre modular design is projected to be built and operated in phases, with Phase 1 operational in 2019 and producing 20,000 metric tons per year and complete production occurring by 2021 producing 200,000 metric tons per year. While current FeedKind production has reached the commercial scale, improvements in metabolic engineering could further enhance this utilization pathway.

A joint venture between Calysta, industrial partner CHAIN Biotech, and the University of Nottingham's Synthetic Biology Research Centre is working on a methanotrophic platform to convert methane into polyunsaturated fatty acids, in particular the popular supplement omega 3.[1] In developmental stages are palatants, probiotics, L-amino acids, and a variety of metabolites.[2] The majority of these commodities will require extensive strain improvements and product recovery engineering.

Intrexon[TM] has developed a commercially viable natural gas–to-liquid bioconversion platform. While Calysta used methanotrophs as the product, Intrexon is using methanotrophs to produce high-value chemicals. They circumnavigated the lack of genome and pathway knowledge by designing novel techniques for library generation and screening—technology that could help advance methanotrophic metabolic engineering.[3] Intrexon has installed existing metabolic pathways into its evolved methanotroph strains and has demonstrated production of isobutanol and farnesene. Isobutanol, an energy-dense, clean-burning drop-in fuel, is the company's initial target and scale-up model. Future products include 1,4-butanediol, a feedstock for plastic, polyester, and polyurethane production. In 2016 the synthetic biology company announced their San Francisco 500-liter pilot plant was operational and later stated that by the end of 2018 they would commercialize isobutanol production.[4] However, they have since retracted their 2018 goal.

The startup company Mango Materials[TM] is focused on converting biogas streams into the biodegradable plastic polyhydroxyalkanoate (PHA) and its derivatives.[5] Mango Materials chose biogas or unrefined syngas as its carbon feedstock, and methanotrophs as its host organism. They are currently working on PHAs for specific applications of textile fibers and caps and closures. Mango Materials is currently in the pilot-scale level of product development and is still in the early stages of modeling its host organism and pathways. Current research in PHA production in nonmethanotrophic organisms has the potential to help pave the way in product recovery engineering for Mango Materials, accelerating their path to commercialization.

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[1] See http://calysta.com/2016/05/scientists-to-use-microbes-and-methane-to-create-sustainable-omega-3/.
[2] See https://www.bio.org/sites/default/files/0830AM-Lori%20Giver.pdf.
[3] See https://www.dna.com/userfiles/files/Engineering%20Microbes%20for%20Commercial%20Products.pdf.
[4] See http://investors.dna.com/2016-03-30-Intrexon-Pilot-Plant-for-its-Methanotroph-Bioconversion-Platform-Now-Operational.
[5] See http://mangomaterials.com/.

Methanotrophs are not limited to being microbial production platforms, as they have also been used in bioremediation, biobleaching, pharmaceutical treatments and reducing methane emissions in landfills. Generating metabolic models, studying carbon flux, and compiling fermentation data are all necessary research areas to industrialize methanotrophs.

A RESEARCH AGENDA FOR CHEMICAL AND BIOLOGICAL UTILIZATION OF METHANE AND BIOGAS

Methane and biogas utilization can be accomplished via chemical or biological approaches. While little waste gas methane is available for nonfuel chemical utilization, as compared to carbon dioxide in waste gas, research breakthroughs in methane utilization to higher-carbon-number products could displace fuel use of methane, making available very large quantities of feedstock. Few industrial processes have emerged for direct conversion of methane to nonfuel chemical products, despite decades of research. To advance methane and biogas conversion processes, more research is needed to improve existing catalysts, as well as to control the selectivity and stability of the methane-derived products to increase product yields. Additionally, separation and purification of biogas may be required depending on the desired product. For biological utilization of methane, methanotrophs have received significant attention; however, there are challenges associated with microbial fermentation, such as the risk of contamination, the buildup of toxic intermediates, and high-cost additives, such as nucleic acids. Better capability to characterize the metabolic pathways downstream of methane assimilations will create more accurate metabolic models.

Chemical Barriers to Commercialization

Stages of development and key barriers for various chemical utilization approaches for methane and biogas are shown in Figure 6-2 and Table 6-1.
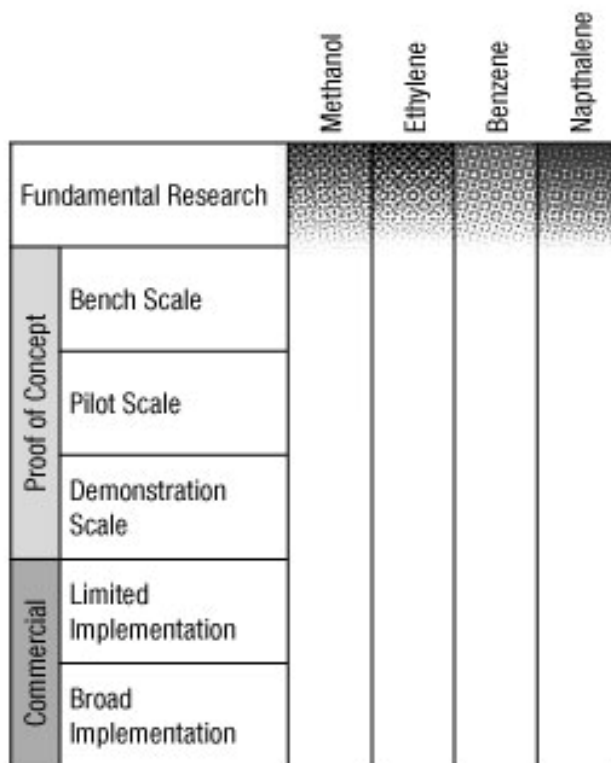
FIGURE 6-2 Stages of research activity for target products of chemical utilization of methane and biogas waste streams. The higher density on the diagram indicates larger amounts of research activity in that stage. Blank areas indicate little or no research activity in that stage for a given product, indicating gaps in research activity.

NOTE: Fundamental research is defined as observation and reporting of fundamental principles of a scientific or engineering process, and formulation of a technology concept. The three proof-of-concept stages are defined as progressively larger-scale reactions to produce product. These include bench-scale processes where critical functions are proved and components or systems are validated in a laboratory environment and at a laboratory scale. Pilot plant scale is defined as a system validated in a relevant environment and at an engineering scale. Demonstration plant scale is defined as a full-scale system demonstrated in a relevant environment. Commercial-limited is defined as an actual system operating at a stage where product is being sold in the market in limited areas with specific advantageous geographical, regulatory, or other factors. Commercial-broad is defined as an actual system operating at a stage where product is sold in the market with opportunities not limited to specifically advantaged locations.

TABLE 6-1 Key barriers for commercialization of the products from Figure 6-2.

Product	Key Barriers
Methanol	Selectivity and stability of methane-derived product, turnover frequency and turnover numbers, catalyst stability
Ethylene	Reaction engineering
Benzene	Reducing the need for harsh reaction conditions, yield
Napthalene	Reducing the need for harsh reaction conditions, yield

Chemical Utilization Priority Research Areas

Catalyst Development

Research is needed to improve existing catalysts or discover entirely new catalysts for methane or biogas conversion. There are few examples of catalysts that are viable on a large scale and this is a high-priority research need.

System Engineering and Reactor Design

Improving the efficiency of methane conversion chemistry would be aided by the integration of catalysts with the most efficient reactor technology. For example, the integration of methane conversion catalysts with reactors that allow for the efficient removal of products which need to be formed at low conversion for thermodynamic reactions would be beneficial. Similarly, separation challenges can be mitigated by developing reactor designs which improve conversion per pass.

New Targets for Methane Conversion

Research exploring methane conversion into commodity chemicals has traditionally focused on a relatively small number of molecules, as outlined in this chapter. The identification of other nontraditional targets and subsequent catalyst development could have transformative impacts.

Biological Barriers to Commercialization

Stages of development and key barriers for various biological utilization approaches for methane and biogas are shown in Figure 6-3 and Table 6-2.
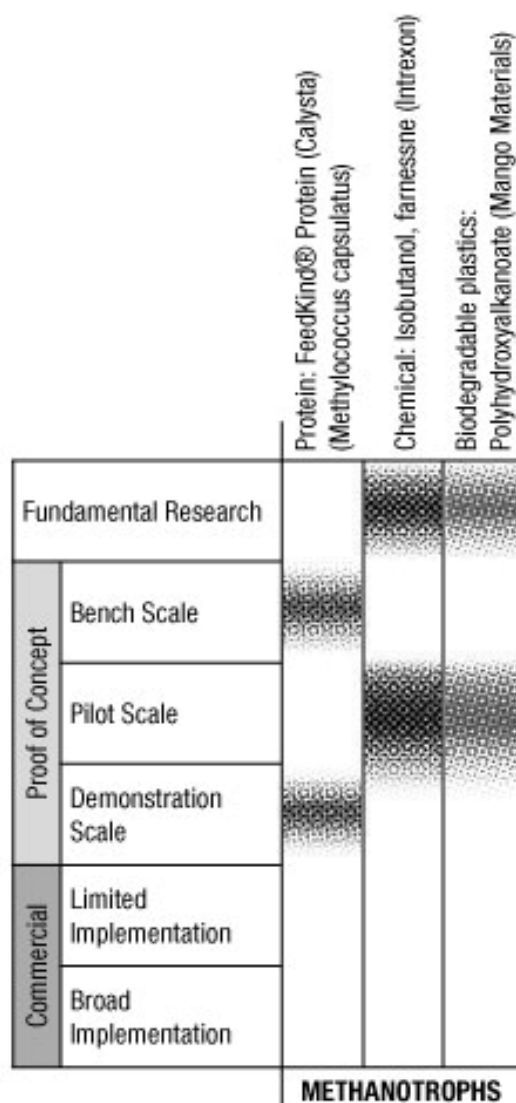
FIGURE 6-3 S Stages of research activity for target products of biological utilization of methane and biogas waste streams. The higher density on the diagram indicates larger amounts of research activity in that stage. Blank areas indicate little or no research activity in that stage for a given product, indicating gaps in research activity.

NOTE: Fundamental research is defined as observation and reporting of fundamental principles of a scientific or engineering process, and formulation of a technology concept. The three proof-of-concept stages are defined as progressively larger-scale reactions to produce product. These include bench-scale processes where critical functions are proved and components or systems are validated in a laboratory environment and at a laboratory scale. Pilot plant scale is defined as a system validated in a relevant environment and at an engineering scale. Demonstration plant scale is defined as a full-scale system demonstrated in a relevant environment. Commercial-limited is defined as an actual system operating at a stage where product is being sold in the market in limited areas with specific advantageous geographical, regulatory, or other factors. Commercial-broad is defined as an actual system operating at a stage where product is sold in the market with opportunities not limited to specifically advantaged locations.

TABLE 6-2 Key barriers for commercialization of the products from Figure 6-3.

Platform	Product	Key Barriers
Methanotrophs	*Protein:* FeedKind® Protein (Calysta) *(Methylococcus capsulatus)*	Social acceptability of GMO limits additional genetic engineering
	Chemical: Isobutanol, farnesene (Intrexon)	Scalability
	Biodegradable plastics: Polyhydroxyalkanoate (Mango Materials)	Scalability, product recovery

Biological Utilization Priority Research Areas

Bioreactor and Cultivation Optimization

Technologies concerning system design for efficient methane solvation, mass transfer, and delivery, as well as dewatering, harvesting and product isolation, and water and nutrient management and recycling remain primary challenges at scale and merit additional research efforts. Improved culture monitoring technologies will also be essential for scale-up applications. Advancement of methane utilization methods may require novel bioreactor design in order to incorporate new feedstocks or hybrid fermentative systems and improve safety. Reactors that capture and reuse unused methane should be explored, as well as pairing reactors with technologies that utilize CO_2.

Genome-Scale Modeling and Metabolic Efficiency

In-depth computational modeling, genetic manipulation, biochemical validation, and fermentative demonstration will be required to create more accurate metabolic models and improve metabolic flux, including methane uptake and incorporation, efficiency, metabolic streamlining, and product accumulation. Research is needed to characterize metabolic pathways downstream of methane assimilations. These pathways are currently unknown or poorly understood.

Bioprospecting

The identification and characterization of new species with unique attributes, such as methane uptake, product profiles, conversion efficiency, and environmental tolerance, will be necessary to facilitate biomass production in diverse geographic locations and produce select products.

Valorization of Co-Products

Given the robust efficiencies of microalgae for protein and oil production, continued studies and certification processes will be required to valorize co-products for feed and food applications.

Genetic Tools

Genetic tools for engineering of nonphotosynthetic biomass organisms remain underdeveloped. Expansion of tools for genetic incorporation, selectable markers, promoter elements, protein folding and stability, and posttranslational control will be needed to develop robust platforms.

Products

Opportunities may be found in the development of new products for unmet needs in commodity and specialty chemicals as well as nontraditional products.

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7

Enabling Technologies and Resources

The committee collectively describes materials and processes that are required to utilize carbon waste streams at large scale (gigatons of carbon per year) as enabling technologies and resources. To accomplish a net life-cycle reduction of greenhouse gas emissions to the atmosphere, many carbon utilization technologies will require low- or zero-carbon sources of electricity, heat, and energy-carrying materials. Additionally, the waste streams will need to be purified, processed, and transported. The following chapter discusses the enabling technologies and resources required to utilize carbon waste streams.

ENABLING TECHNOLOGIES

Waste Gas Separation and Purification

Waste gas streams are heterogeneous in their composition, and this heterogeneity poses challenges for carbon utilization. Sources of carbon dioxide range from highly concentrated by-products of chemical manufacturing to relatively dilute flue gas streams from power plants with nitrogen oxide, sulfur oxide, and other contaminants. Methane in waste gas ranges from widespread biogas from waste treatment and landfills, containing contaminants such as hydrogen sulfide, oxygenated hydrocarbons, and siloxanes, to methane-contaminated air from sparse coal mine vents. Composition of the waste gas varies not only by the process generating the waste stream but also by the condition of the process (e.g., the level of activity in a coal mine or the amount of moisture available in a landfill), sometimes varying on a daily or hourly basis and sometimes in unpredicted ways. To utilize methane and carbon dioxide mixed with other gases in carbon waste streams, utilization processes must be developed that can tolerate variable and mixed streams, or waste gas separation and purification will need to be widely deployed. For many utilization technologies, which are at early stages of development, the required purity of carbon dioxide or methane is unknown. As utilization technologies develop, it will be critical to identify acceptable purity levels for carbon utilization process feedstocks that meet process requirements and minimize costs. In some cases it may be desirable to perform separation and purification of waste gases prior to transporting carbon dioxide or methane to utilization processes because of economies of scale or other factors. In other cases it may be desirable to integrate the waste stream purification into the utilization process. Because of this uncertainty in the separation and

purification needs of carbon utilization technologies, only the general need for these technologies is certain. Specific research and development needs will emerge over time. This section provides a broad overview of separation technologies and the types of research advances that might be required. Separation science is the focus of an ongoing Academies study (Committee on a Research Agenda for a New Era in Separations Science[1]) and, although it will not be covering specific applications like carbon waste separation, key fundamental areas will be discussed that can advance separations, regardless of application.

As discussed in Chapter 2, methane and carbon dioxide waste gases are generated in different locations, with different chemical characteristics, and with different requirements for use, leading to different needs for waste gas separations and purification. Methane waste gas streams from the oil and gas sector tend to be relatively concentrated, on the order of 70-95 percent methane, and have the fewest separation needs. Contaminants include ethane, propane, butanes, and other light hydrocarbons, and in some cases H_2S or CO_2.

Biogas from landfills and wastewater digesters are typically a mix of methane and CO_2, at approximately 50 percent methane and 50 percent CO_2 for the landfill gas, and 70 percent methane and 30 percent CO_2 for the wastewater digester gas. Biogas separation needs can be approached from the methane or CO_2 separation standpoint, and the biogas can also be used in a mixed state, as discussed particularly in Chapter 6. While methane waste gases associated with oil and gas production are typically relatively clean of impurities that hinder utilization, biogas sourced from landfills can include contaminants such as halogenated organic compounds, hydrogen sulfide, mercury-containing compounds, siloxanes, ketones, and sulfur-containing species and that sourced from digesters often contains problematic impurities such as ammonia, hydrogen sulfide, and a variety of organic compounds including organic sulfides, disulfides, C4 to C7 aldehydes, amines, quinoline, dimethylpyrazine, and organic acids, along with lesser amounts of C4 to C7 alcohols, ketones, aliphatic hydrocarbons, and aromatic compounds (NRC, 2003). Coal mine vents typically make up only very small percentages of methane, and face challenges in methane concentration.

Widely used cleanup technologies for methane or carbon dioxide can be generally divided into four classes: (1) chemical absorption with basic media, normally aqueous, or physical absorption in liquid media; (2) application of low temperatures (cryogenic); (3) adsorption on a solid surface, followed by later removal under a temperature and/or pressure change; and (4) membrane separation.

Within each of these categories are a number of specific processes, distinguished by the solvent, sorbent, or membrane used; processing conditions; and resulting purity of the desired products(s). Selection of a specific process is highly dependent on the specific gas stream to be treated and the conditions required for the purified gas stream. Each cleanup system has unique features, advantages, and disadvantages which include energy consumption, capital costs, and the production of by-product streams of contaminated cleanup media for disposal.

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[1] Available at http://nas-sites.org/dels/studies/separations/ (accessed August 1, 2018).

Chemical Absorption with Basic Solutions

A wide variety of amine solutions have been used to absorb carbon dioxide. Once the carbon dioxide is absorbed, the amine-containing solution must be regenerated or stripped to remove and recover the carbon dioxide so that the solution can be reused. Elevated pressure and low temperatures aid the absorption, while the opposite conditions—higher temperatures and lower pressure—are used to remove the carbon dioxide. Regeneration of the aqueous amine solution is energy intensive. Common problems for these systems include corrosion of the mechanical systems and degradation of the solution over time. Scrubbing technology was developed initially to remove acidic gases from natural gas and to purify hydrogen and synthesis gas streams. In these cases the feed gas is typically available at elevated pressure. In many CO_2 waste gases, such as flue gas from a power plant or cement kiln, the gas stream is only available at slightly above atmospheric pressure. Additional energy would be required to raise the gas pressure to a level sufficient for effective treatment. In addition, many of the CO_2-containing waste streams also contain oxygen, which accelerates amine degradation.

Physical Absorption with Solvent

If the waste gas stream is available at sufficient pressure, a physical solvent can be used in which the gas dissolves (but does not chemically react). The gas-rich solvent is circulated to a low-pressure vessel where the dissolved gas is released and removed. Several well-developed commercial systems have been used extensively, particularly for purifying high-pressure hydrogen streams and synthesis gas. Purisol® (using N-methyl-2-pyrrolidone), Rectisol® (using methanol), and Selexol® (using a mixture of glycol ethers) are typical examples. An advantage of such systems is that they do not require heat to regenerate the solvent, they have less corrosion and solvent degradation, and they have smaller waste streams for disposal. However, they produce a lower-pressure product gas than the feed stream, which may or may not be desirable, depending on the application.

Low-Temperature Purification

Low-temperature purification is an effective means to produce a very-high-purity (>99 percent) CO_2 or methane stream. The process is energy intensive, resulting in high costs. In addition, other compounds in a typical waste stream such as water and hydrocarbons can freeze, plugging the cryogenic equipment and interfering with the separation.

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Adsorption on Solid Media

Molecular sieves have been developed and commercialized to separate a wide variety of components in mixtures, including CO_2. The precise sieve composition and pore size is tailored to capture a target gas molecule and remove it from a mixture. The most common application of this technology is called pressure swing adsorption (PSA). PSA has been applied to hydrogen purification from steam-methane reforming, among other chemicals, producing a very pure hydrogen product and a carbon dioxide stream. In many cases, multiple adsorbents are used within the same vessel to remove other minor impurities such as water and ammonia. The hydrogen recovery depends on the desired purity and the nature of other contaminants. Carbon dioxide waste streams pose additional challenges for this technology since they are typically available at modest pressure so additional compression may be required. A variation of PSA is a temperature swing adsorption process in which the solid is heated to remove the adsorbed component rather than changing the pressure.

Membrane Separation Processes

A variety of porous membrane materials have been developed over the past 40 years for gas-phase separations. Current materials include a multitude of polymers with specific functional groups attached. The first commercial process developed by Monsanto in the 1980s for purifying hydrogen, now owned and licensed by Air Products,[2] is currently used in a number of hydrogen manufacturing plants. Membrane separation depends on maintaining a pressure and concentration differential on the two sides of the membrane to provide a driving force for the separation. Membrane systems suffer from relatively poor mechanical strength and sensitivity to impurities in the feed stream. The challenges for future, large-scale use of membrane separations remain (1) developing membrane materials that exhibit high permeability (throughput) while maintaining high selectivity and (2) improved mechanical strength.

Waste Gas Transportation and Delivery

The sources of carbon waste streams and other required inputs for waste stream utilization are often not co-located. In the United States, the Greenhouse Gas Reporting Program (GHGRP) hosted by the Environmental Protection Agency (EPA) tracks facilities emitting greenhouse gases over 25,000 metric tons of carbon dioxide equivalent (MMT CO2e), which includes many facilities that are sources of carbon waste streams. Figure 7-1 depicts the location and total reported emissions from each facility that reported directly to GHGRP. Waste carbon is emitted by a variety

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[2] Available at http://www.airproducts.com/Products/Gases/supply-options/prism-membranes.aspx (accessed August 1, 2018).

of sectors, including power plants, petroleum and natural gas systems, refineries, chemical facilities, and waste management facilities. The size and distribution of these waste carbon sources and proximity to infrastructure must be considered to enable local and nonlocal utilization. It will be important to also consider the locations of courses and utilization technologies when constructing new pipelines to transport carbon waste gas streams.
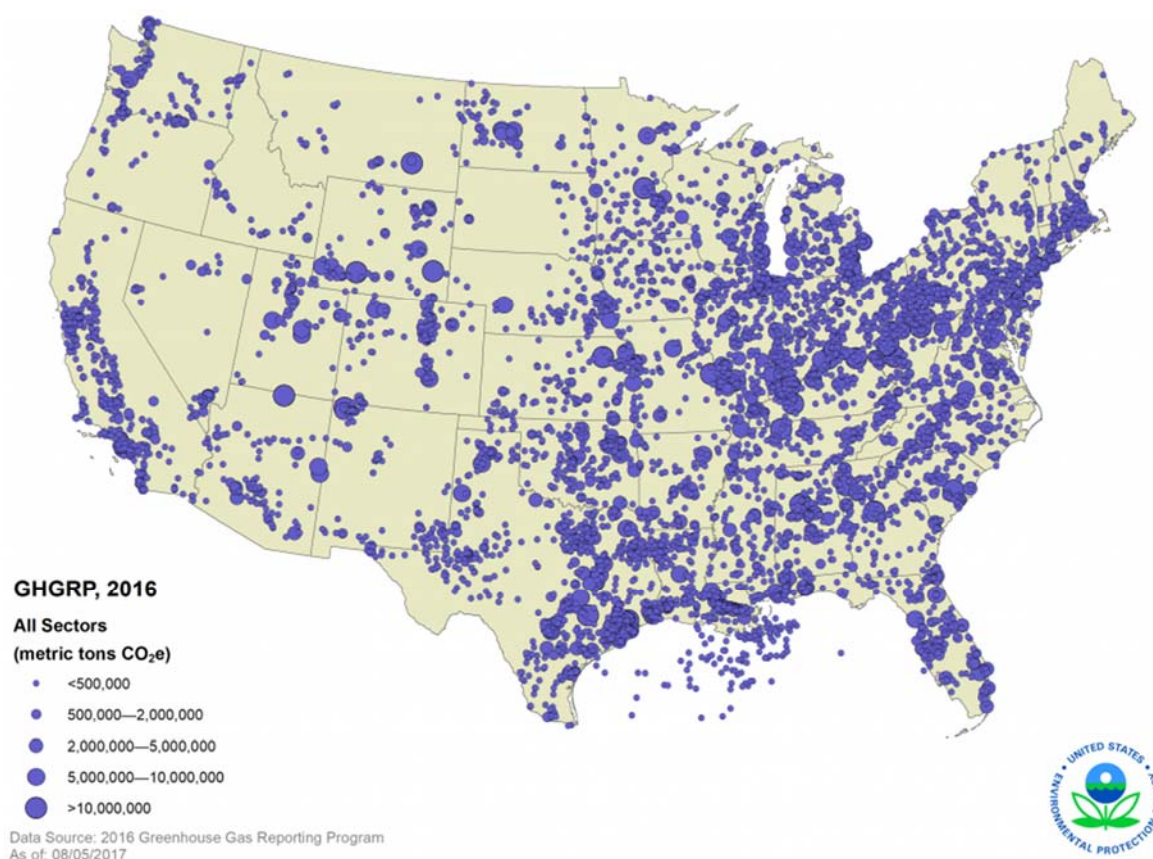
FIGURE 7-1 Greenhouse gases in the United States, 2016. SOURCE: Greenhouse Gas Reporting Program Data Sets (EPA, 2016).

Carbon Dioxide Pipelines

Carbon dioxide transportation pipelines are used to move carbon dioxide from points of production (either waste gas or mineral sources) to utilization sites. There are 50 individual CO_2 pipelines that have been constructed in the United States with a combined length of more than 4,500 miles (NETL, 2015). The vast majority of the CO_2 pipeline system (see Figure 7-2) is dedicated to enhanced oil recovery, and a small fraction is used for other industrial uses such as the beverage industry. Roughly 80 percent of the transported CO_2 is from geological sources and the remaining 20 percent from industrial sources including gas processing plants. Because of these

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limited sources and utilization pathways, the availability of pipeline-quality carbon dioxide is limited both in magnitude and by location.
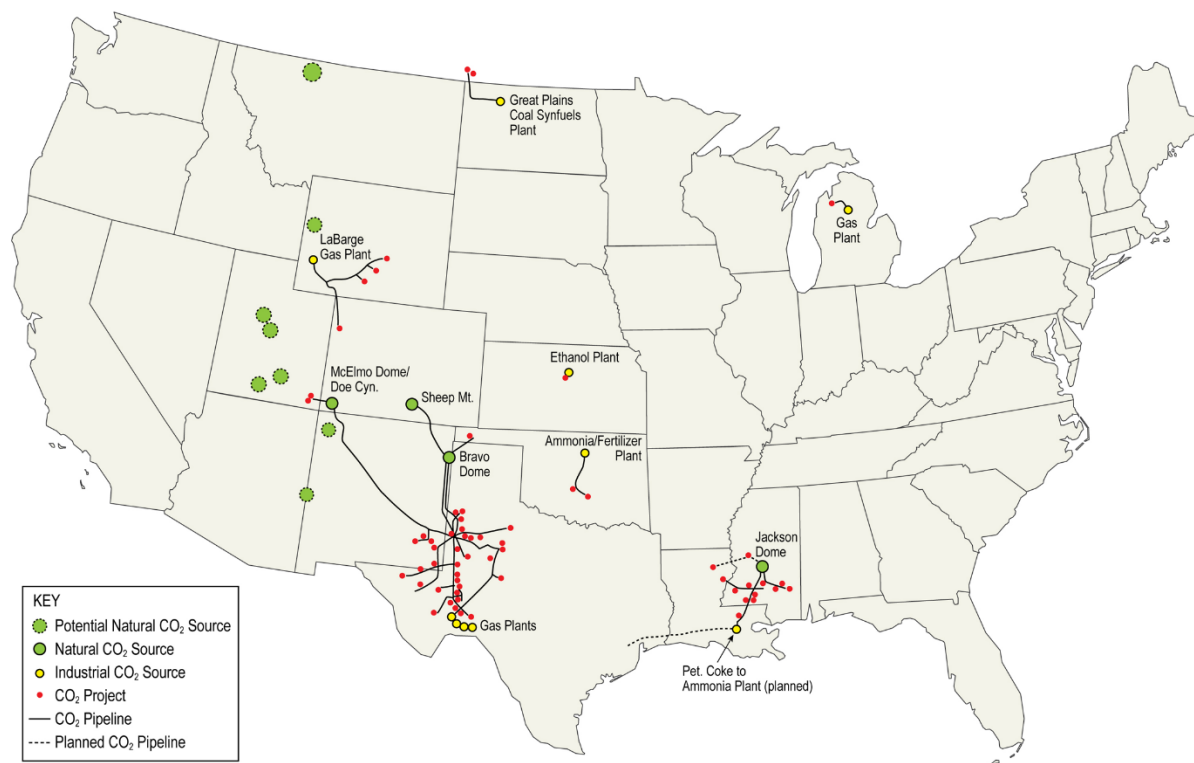
FIGURE 7-2 Carbon dioxide–enhanced oil recovery pipeline infrastructure. SOURCE: NETL, 2010.

Methane Pipelines

In comparison to the CO_2 pipeline infrastructure, the natural gas pipeline network in the United States is very large and provides gas transportation services to each of the lower 48 states. There are three different categories of national gas pipeline systems: gathering, transmission, and distribution. Gathering pipelines transport gas from wells where it is produced to gas processing and purification and transmissions systems, which then bring the gas to storage facilities, customers, and distribution systems.

The United States has more than 320,000 miles of natural gas gathering and transmission pipelines and more than two million miles of gas distribution pipelines (see Figure 7-3). The purity of gases that are permitted to be transported is specified by pipeline operators and can vary depending on the type of pipeline and location of the pipeline (McKaskle, 2014).[3]

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[3] Available at https://www.eia.gov/todayinenergy/detail.php?id=36494 (accessed October 10, 2018).

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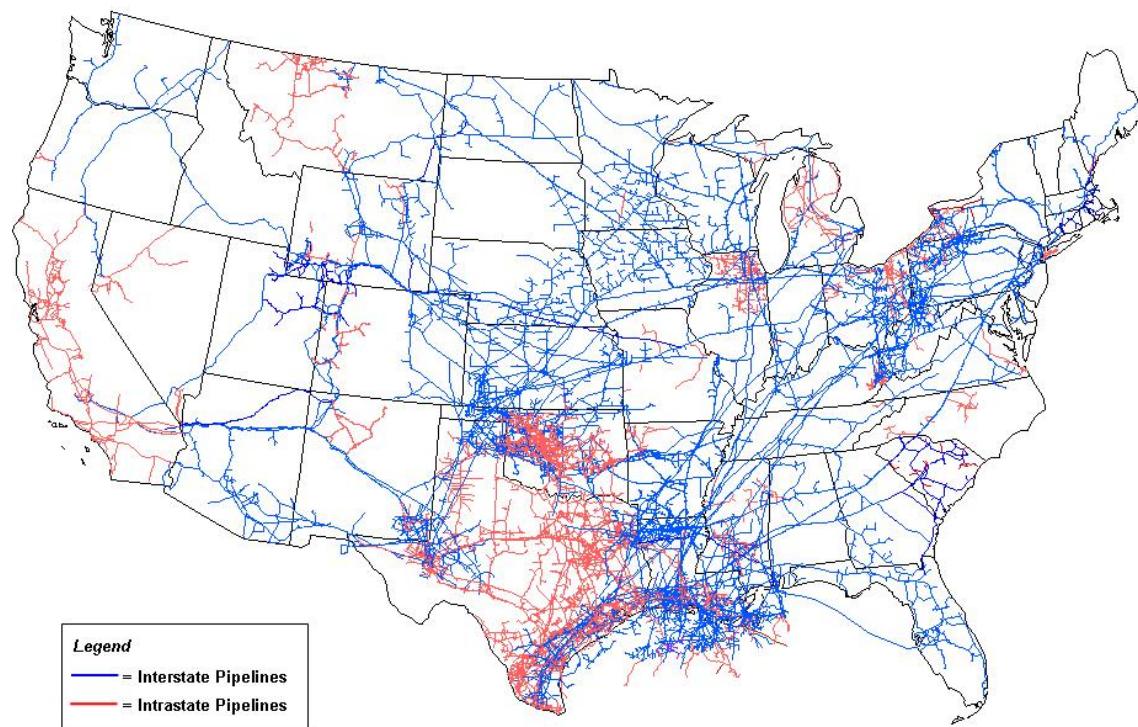
FIGURE 7-3 U.S. Natural Gas Pipeline Network 2009. SOURCE: U.S. Energy Information Administration.[4]

ENABLING RESOURCES FOR CARBON DIOXIDE UTILIZATION

After delivering the purified waste gases to the point of utilization, other energy and material requirements are often needed to support carbon utilization. Some key enabling resources to support carbon dioxide utilization are hydrogen, electricity, and heat, each of which serve as energy carriers. Methane utilization often also requires electricity and heat. Though many processes in the chemical and biochemical industries require such inputs, they are particularly salient for carbon waste stream utilization where a net reduction of greenhouse gas emissions is a requirement.

Hydrogen Sources

There is a national-scale mismatch between the magnitude and location of hydrogen from low-carbon resources and the magnitude and location of the majority of carbon waste streams. Enabling technologies for generating hydrogen and transporting hydrogen are thus integral to widespread carbon waste stream utilization. Hydrogen can be produced from a diverse range of

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[4] Available at http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/ngpipeline/ngpipelines_map.html (accessed October 10, 2018).

resources. Most hydrogen is produced by the steam reforming of methane (see Figure 7-4), but to achieve net carbon utilization, hydrogen used as a reactant for carbon waste stream utilization must be produced from low-carbon resources such as wind, solar, and biomass (see Figure 7-5). Hydrogen can be produced by electrolysis from renewable electricity and water, but the cost of producing hydrogen with this route is relatively high at large scales.
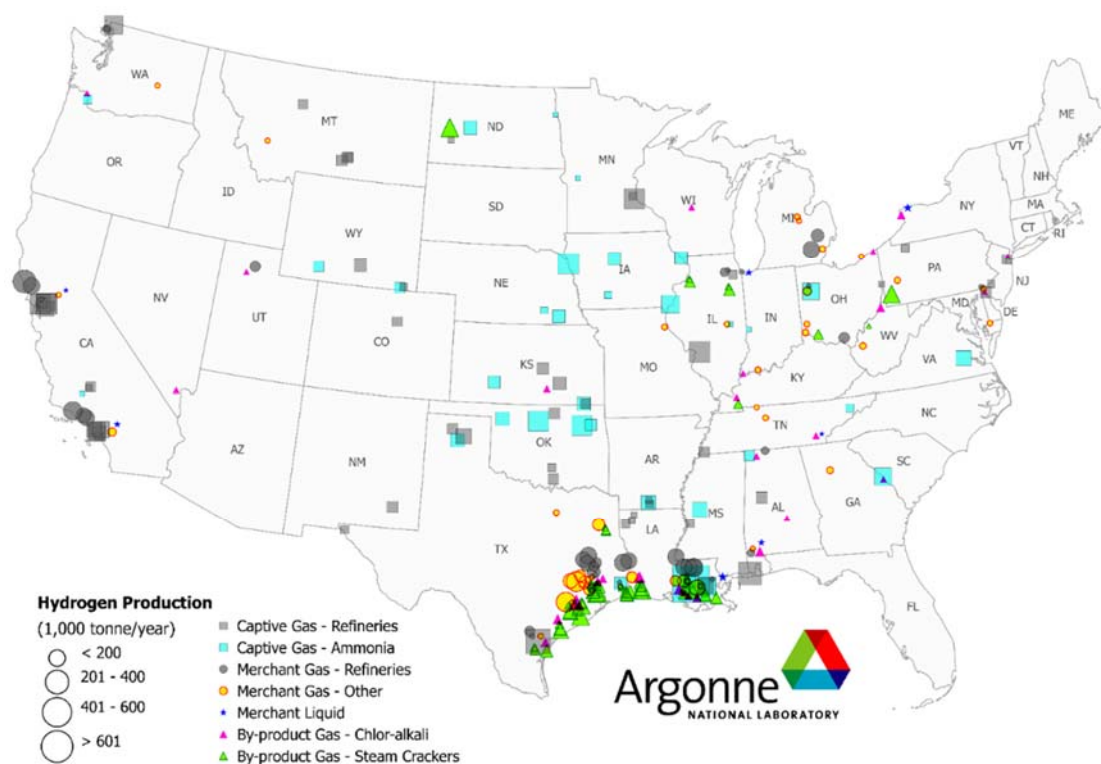
FIGURE 7-4 Industrial hydrogen production facilities in the United States. SOURCE: Argonne National Laboratory.

Hydrogen can be produced (1) at or near the site of use in distributed production, (2) at large facilities and then delivered to the point of use in central production, or (3) at intermediate-scale facilities located in close proximity (25-100 miles) to the point of use in semicentral production (see Figure 7-6). Distributed production is a term used when small units of hydrogen are produced where it is needed. Centralized production is a term used to describe large central hydrogen production facilities (50,000 kg/day) and oftentimes requires more capital investment as well as substantial hydrogen transport and delivery infrastructure. Semicentral production descibes intermediate-size hydrogen production facilities (5,000-50,000 kg/day) located in close proximity to the point of use. These facilities minimize hydrogen transport costs and infrastructure.[5]

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[5] Available at https://energy.gov/eere/fuelcells/central-versus-distributed-hydrogen-production (accessed August 2, 2018).
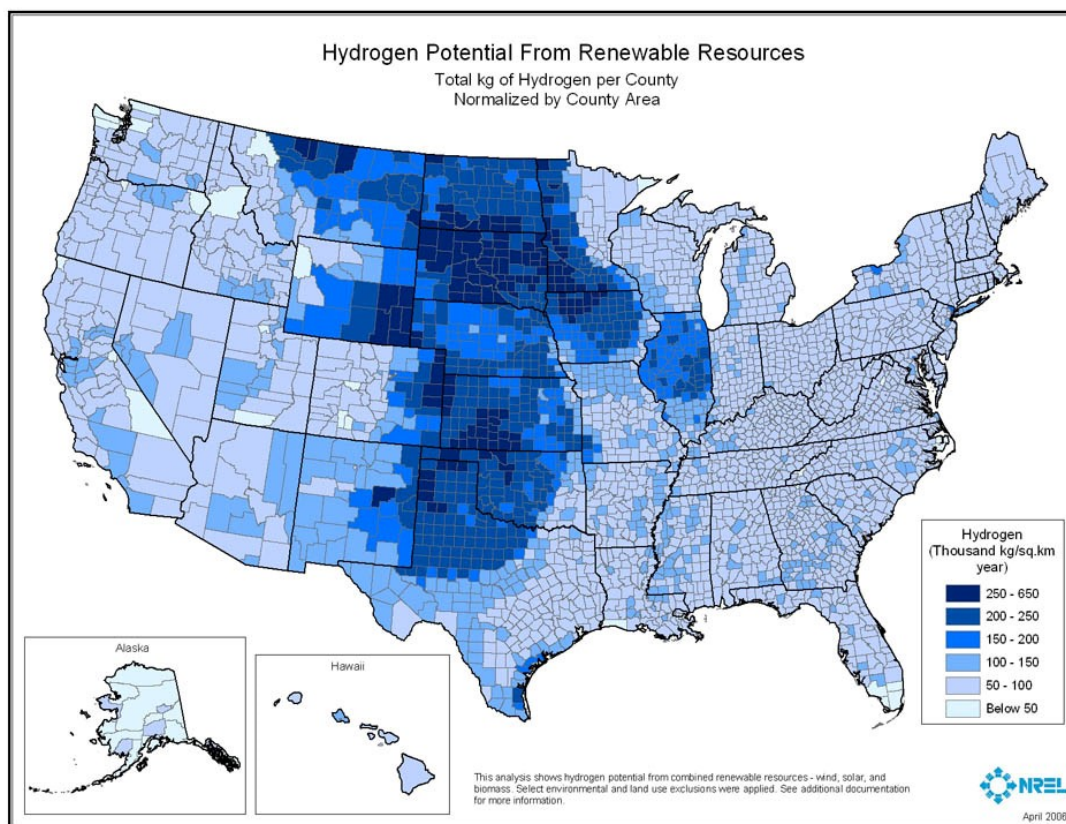
FIGURE 7-5 The potential sources of hydrogen from renewable resources, including wind, solar, and biomass. SOURCE: NREL, 2006.
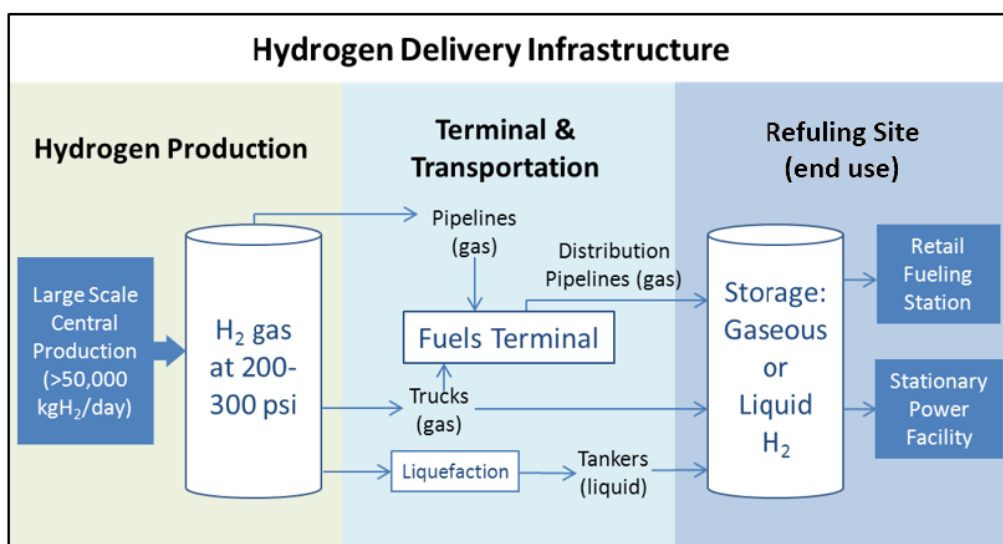
FIGURE 7-6 Illustrative example of the hydrogen delivery infrastructure. SOURCE: U.S. DRIVE, 2013.

Electricity

Converting carbon dioxide to fuels and chemicals can require a large amount of energy. Reducing carbon dioxide emissions through carbon dioxide utilization will only be possible if the electricity and, in some cases, the thermal energy inputs are from renewable or low-carbon resources. The reduction of costs for renewable sources such as solar and wind has enabled low-cost, near-zero-carbon electricity abundant in volume and over large areas (see Figure 7-5). In some markets, electricity is available, at times, at very low or even negative prices.[6] When low-carbon energy sources are highly variable in their output, such as for solar and wind resources, compensating for intermittency can impose additional costs on carbon utilization processes. Many facilities will use electricity from the electric grid, which will mix the sources of electricity and will reduce dependence on any one generation source. A deeper discussion of assessing emissions impacts of carbon utilization technologies is available in Chapter 8.

Heat

High-temperature (>900ºC) heat can be used to convert CO_2 into value-added products. The classic example is dry reforming of methane (see Chapter 6) via the following reaction:

$$CH_4 + CO_2 \leftrightarrow 2\,CO + 2\,H_2 \left(\Delta H^O_{298K} = +247\text{ kJ mol}^{-1} \right) \qquad \text{(Eq 10)}$$
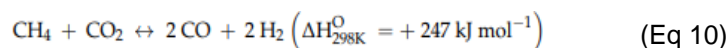
This reaction is highly endothermic with a ΔH value of +247 kJ/mol. Similarly, the reverse water gas-shift reaction (Eq 11) is mildly endothermic, with a ΔH value of +41 kJ/mol:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \left(\Delta H^O_{298K} = +41\text{ kJ mol}^{-1} \right) \qquad \text{(Eq 11)}$$
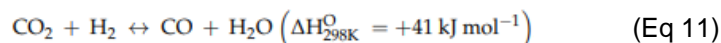
The dry reforming reaction is more relevant for conversion of CO_2 into syngas as it does not require any hydrogen. The high-temperature heat needed for the dry reforming reaction can potentially be obtained from a number of industrial sources. Nuclear power plants can provide relatively inexpensive low-carbon waste heat at high temperatures, but this will require locating the CO_2 conversion process in the vicinity of a nuclear plant, which may not be always possible. There have been recent advancements to couple the export power, heat, and hydrogen of small modular nuclear reactors with evolving advanced manufacturing technologies for further energy and carbon savings.

Other sources of this waste heat could be exhaust gases from gas turbines, electric arc furnaces in the steel industry, aluminum melting furnaces, glass furnaces, and other sources. Most

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[6] FUTURE Act at 45Q(f)(2), available at https://www.congress.gov/bill/115th-congress/senate-bill/1535/text (accessed August 2, 2018).

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oil refineries and petrochemical plants also have some waste heat available. Generally, some of this waste heat is recovered in recuperators to produce steam and/or power, but the efficiency of this conversion is quite low. Also, some of these waste exhaust gases from the steel and glass industries contain fine particulates and/or condensable vapors which may be difficult to handle without significant capital equipment.

FINDINGS

A variety of enabling technologies and resources are required for widespread carbon utilization with net greenhouse gas emissions reduction. These include separation and purification, transport, and low-carbon sources of heat, electricity, and energy-carrying materials such as hydrogen. Because the needs of carbon utilization processes are still emerging, a specific research agenda for these enabling technologies and resources is unclear. Therefore, as carbon utilization technologies emerge, the integration of the research agenda for carbon utilization and enabling technologies and resources must be considered.

> **Finding 7-1** Depending on the carbon utilization technology, enabling technologies and infrastructure such as waste gas cleanup, extensive energy inputs, or inputs of reactive gases (e.g., hydrogen) and co-location of waste streams may be required.

> **Finding 7-2** The development and deployment of systems for carbon utilization will require research advances and deployment of enabling technologies and infrastructure for energy and other resources, in addition to advances in the conversion of carbon waste to useful products.

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8

Life-Cycle Assessment of Carbon Utilization

Life-cycle assessment (LCA) is a technique used to evaluate energy, water, and materials (e.g., chemicals and metals) inputs, outputs, and emissions over the life cycle of a process or product. The International Standards Organization (ISO, 2006) describes the principles and framework of LCA, which take into account the acquisition of raw materials, raw material conversion to product, transportation and distribution of product to point of sale and/or distribution, product use, and product disposal stages of a product's life cycle.

LCA is particularly relevant for evaluating carbon utilization. While carbon utilization technologies take up CO_2 and methane that would otherwise be emitted, the conversion of these greenhouse gases into products consumes energy and materials. Energy and materials consumption results in emissions of greenhouse gases which may or may not, on net, reduce overall emissions as a result of using the carbon utilization technology (Bruhn et al., 2016; von der Assen et al., 2013, 2014). The net greenhouse gas emissions of the carbon utilization process are not the only emissions to consider, however. A key consideration is whether the CO_2- or methane-derived product will displace another product. For example, the fabrication of a polymer, using carbon dioxide as one of several building blocks, may on net emit greenhouse gases, since energy and other materials used in making the polymer may result in greater emissions of greenhouse gases than are taken up in the polymer by using carbon dioxide. If, however, that polymer fabricated with carbon dioxide displaces a polymer with greater life-cycle greenhouse gas emissions, the net effect is a reduction in emissions. This product displacement can be a significant component of the overall greenhouse gas benefit of carbon utilization technologies. For example, as described in Box 10-2 (see Chapter 10) for polyols produced by Covestro, the greenhouse gas emissions from the waste gas utilization process are 2.6-2.9 kg CO_2e/kg (not net negative); however, they result in emissions that are 0.4-0.6 kg CO_2e/kg less than the production of conventional polyols, making the overall waste gas utilization and product displacement net negative. The factors used by the committee in this report to define "net-negative life-cycle greenhouse gas emissions" for waste gas utilization are described in Box 8-1.

Box 8-1

Factors for Net-Negative Life-Cycle Greenhouse Gas Emissions

Products from waste gas utilization processes have the potential to be net-negative greenhouse gas (GHG) emissions, or a carbon sink, if the amount of GHG emissions over the life cycle of the product is less than the GHG content of the waste gas stream. A net-negative emissions product would likely be produced with process inputs that are minimally GHG intensive on a full fuel-cycle basis, such as electricity and hydrogen produced from solar or wind, and would be long lived such that the carbon they contain is retained in the product for a long time.
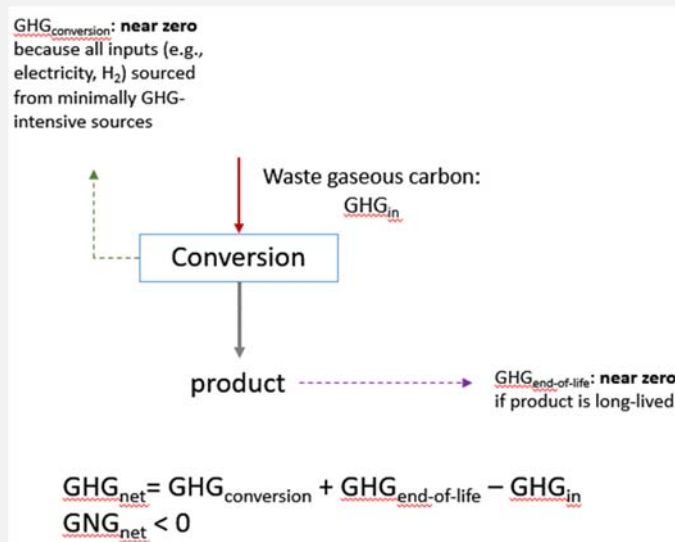
On the other hand, fuels, chemicals, and materials produced from waste gas carbon may be less GHG intensive over their life cycle as compared to a product directly or functionally displaced, resulting in GHG reductions as compared to today's (business-as-usual) technology. In this report, the committee considered both technologies that lead to net-negative greenhouse gas emissions and technologies that lead to net greenhouse gas emission reductions, when displacement of business-as-usual technologies is included.
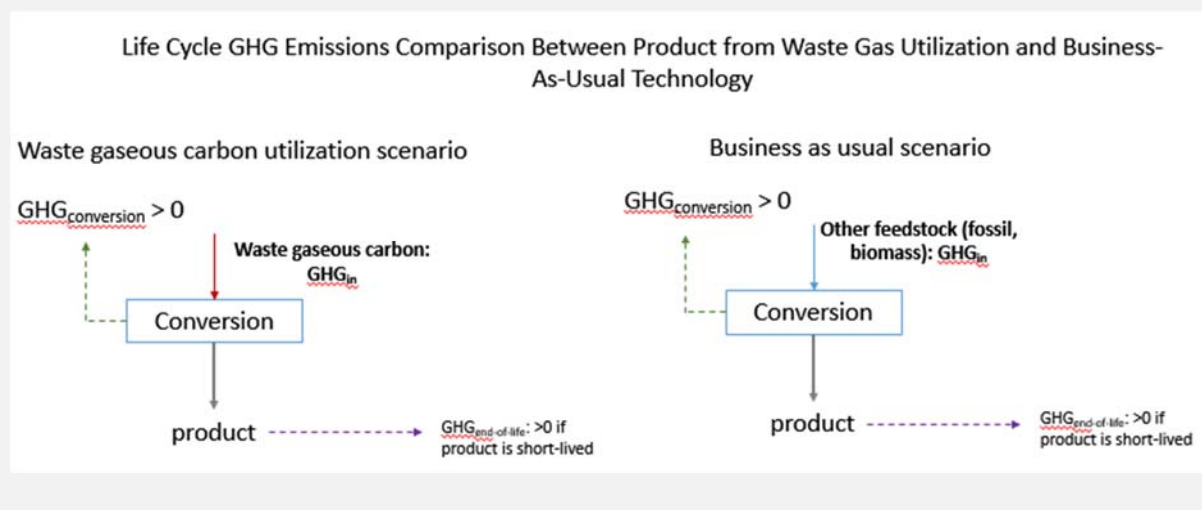
    In addition to greenhouse gas mitigation, carbon utilization technologies can have other benefits (Bruhn et al., 2016), including increased energy and chemical feedstock security, reduced

risk of environmental damage from feedstock extraction, and other factors including enhancing a circular carbon economy. Furthermore, discovery of new reactions and processes associated with carbon utilization may lead to development of new processes that are less hazardous than those they replace.

LCA can be used to address a variety of important questions regarding carbon utilization technologies:

- Does converting waste gases to a product (e.g., fuels, polymers, chemicals, or building materials) emit more greenhouse gases than are sequestered in the product?
- If there is a conventional way to make the product, is the greenhouse gas utilization route to the product less energy, emissions, water, and pollutant intensive?
- Are there trade-offs among different energy and environmental impacts of carbon utilization technologies? For example, perhaps a carbon utilization route is less energy intensive than a conventional route to a product but more water intensive.
- What are the energy and environmental impact drivers of carbon utilization technologies and where are the most significant research and development efforts needed to curtail them? How do these drivers shift if a different source of waste gas is used or a different conversion technology applied?
- What are the energy consumption and environmental burdens associated with preparing waste gas for use (e.g., purified, pressurized, heated, or cooled) from different sources?
- What are environmental impacts of materials widely used in CO_2 utilization routes, including catalysts, energy-carrying materials such as hydrogen, and solvents?
- How would the displacement of conventional routes to products with carbon utilization routes ripple through the supply chain and what are the corresponding energy and environmental impacts?
- Which uses of waste gases (e.g., to chemicals or building materials) offer the greatest net greenhouse gas emissions abatement?

Several recent carbon capture and utilization LCA overviews and reviews (Artz et al., 2017; Cuellar-Franca and Azapagic, 2009; Rahman et al., 2017; von der Assen et al., 2013, 2014) provide a summary of the application of LCA to carbon utilization with some discussion of ongoing issues and research needs. The reviews suggest that the application of LCA in evaluating carbon utilization is expanding rapidly. Notably, whereas in 2013, von der Assen et al. reported only a handful of LCAs of utilization studies regarding chemical production, in 2017, Artz et al. reported a larger number of technologies, including production of dimethyl carbonate, polyols, syngas, formic acid, methanol (solar based, co-electrolysis, and hydrogenation), methane from CO_2, and Fischer-Tropsch fuels. Of liquid fuels produced from waste CO_2, algae-derived diesel has received a great deal of attention (NRC, 2012; Tu et al. 2017; Zhou et al., 2017). LCAs on mineral carbonation have been more limited, with Giannoulakis et al. (2014) providing a summary of key issues associated with this topic relevant to European Union power generation systems.

They describe the importance of process configuration, consideration of transportation of CO_2 versus minerals, and the difference in activation step energy intensity by type of mineral.

While LCA has an important role to play in the evaluation of carbon utilization technologies, there are multiple methodological considerations and details in the application of LCA to carbon utilization technologies that must be carefully addressed if LCA is to provide a consistent and transparent framework for evaluating carbon utilization technologies. Each of these aspects, as described below, should be considered and described transparently when reporting LCA results along with material and energy flow data and sources and assumptions.

FACTORS TO CONSIDER IN LCA OF CARBON UTILIZATION SYSTEMS

System Boundary

The system boundary of an LCA defines which elements of a product's life cycle are under consideration in a given analysis. Figure 8-1 depicts a system boundary appropriate for considering a single carbon utilization technology. In carbon utilization LCA, the system boundary must include the waste gas capture and any pretreatment steps prior to purification in addition to CO_2 compression and transport to the point of conversion, if conversion is not co-located with capture (CO_2 Sciences, Inc., 2016; Cuella-Franca et al., 2014; von der Assen et al., 2013, 2016).
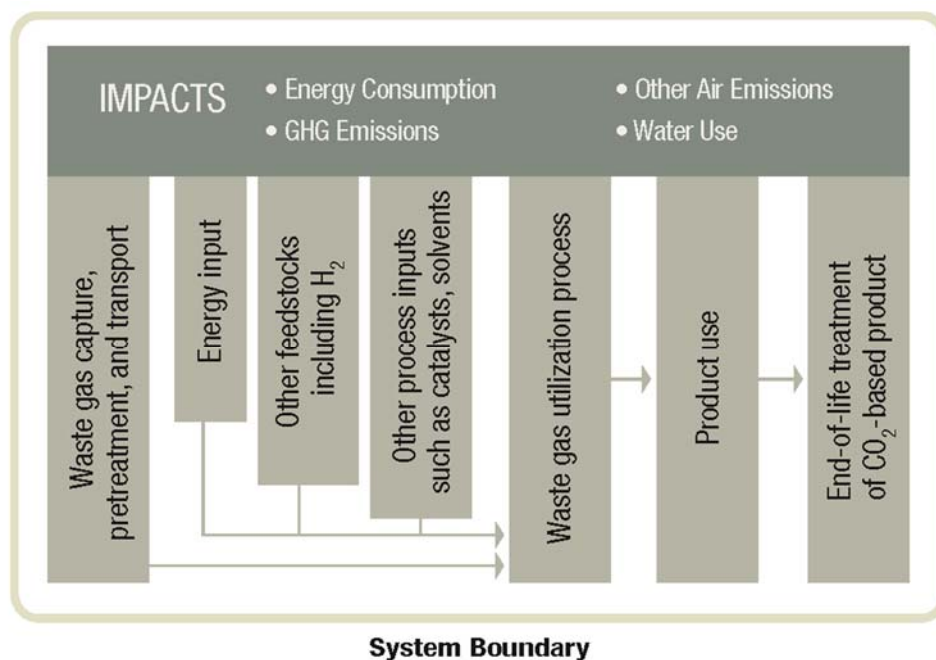
System Boundary

FIGURE 8-1 An illustration of a typical system boundary for a carbon utilization system.

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The LCA should also include the sourcing of additional conversion process inputs such as hydrogen and energy. The origins of both of these inputs are often key determinants of LCA results (Artz et al., 2017; von der Assen et al., 2014). Electricity, for example, can be produced from coal or natural gas power plants (which may in turn be the source of CO_2) or renewable sources. Hydrogen and natural gas can be produced from renewable or nonrenewable resources with differing associated energy and emissions intensities. Other conversion process inputs such as catalysts, adsorbents, and solvents and their production should also be included in the system boundary. The use phase is also an important consideration. In the case of building materials, for example, the performance or amount of material required to achieve a given lifetime of a piece of infrastructure may differ between conventional materials and those made via a carbon utilization technology. The fate of a product at end of life is also a critical aspect of a waste gas utilization product's life cycle within the system boundary, as described later in this chapter. If carbon utilization–based and conventional routes to a common product are to be compared, it is also important to establish an analogous system boundary for the conventional product that takes into account the same factors.

In considering the system boundary, it is also important to consider which energy and environmental impacts will be assessed in the analysis. While energy consumption and greenhouse gas emissions are logical impacts to include in carbon utilization LCA, other impacts including water consumption and air pollutant emissions should not be ignored. However, with the exception of water consumption in the case of algal biofuel (Tu et al., 2017) LCA generally remain unexamined for fuels, chemicals (Artz et al., 2017), and materials produced from waste gaseous carbon.

Functional Units

In a LCA, the functional unit is the basis on which the energy and environmental impacts of a product are compared. With the system boundary described above, if a chemical were the product under consideration, an appropriate functional unit could be a kilogram (kg) of that chemical, especially if an analyst were comparing, for example, methanol produced via a carbon utilization technology as compared to conventional technology. A kilogram of methanol will function equivalently whether produced from CO_2 or via conventional routes. However, materials may be produced from carbon utilization technologies that differ in material structure but offer similar functions as conventional materials and would therefore be considered functional rather than direct replacements. For example, in the case of a carbon utilization–derived building material, a functional unit could be a tensile strength or the ability to bear a given amount of weight over a certain amount of time, and some products derived from carbon utilization processes may be able to achieve those functional properties with less product mass than a conventional material.

A comparison between conventional and carbon utilization pathways is not necessarily confined to a single functional unit. For example, a carbon utilization system consisting of carbon

dioxide captured from a power plant and a carbon utilization process can be viewed as having two products: the electricity generated by the power plant and the carbon utilization product. The system would include coal or natural gas production and conversion to electricity with associated carbon capture and conversion technology. The system boundary would encompass the entire power plant and carbon utilization through the end of the product's life cycle to consider how, on net, CO_2 emissions and other factors vary based on which carbon utilization technology is associated with a power plant. For example, there may be synergies between the electricity generation process and the carbon utilization process if some of the heat normally wasted by a power plant is used to operate the utilization technology.

A key methodological issue in LCA of carbon waste gas utilization systems is the treatment of the energy and emissions intensity of the waste gaseous carbon stream itself. In a case in which CO_2 emitted by a power plant is not used to produce a fuel, chemical, or material, the (unpurified for conversion) CO_2 emissions are assigned to the power plant. When the CO_2 stream is an input into a waste gas conversion process, the CO_2 stream's energy and emissions intensity varies depending upon the analysis approach. For example, the CO_2 stream could still, as above, be assigned to the power plant. Alternatively, it could be burdened only with emissions associated with CO_2 capture and pretreatment, or finally be burdened with emissions associated with sourcing the power plant fuel (e.g., coal mining). von der Assen et al. (2017) provide an overview of the relative burden of preparing CO_2 from European chemical plants, natural gas processing plants, paper mills, power plants, and iron and steel plants. Similarly, Supekar and Skerlos (2014) provide estimates of the energy and environmental impacts of recovering CO_2 from ammonia and ethanol plants, hydrogen plants, and natural gas wells with a market-based allocation approach. Strategies taken for handling the energy and emissions intensity of waste gas and other process inputs that would otherwise be wastes are under development. For example, the Renewable Fuel Standard (RFS) treat biogas used to produce compressed natural gas (CNG), liquefied natural gas (LNG), or electricity as carbon neutral (burden free). The burdens assigned to the biogas are those for upgrading it and processing or converting it to CNG, LNG, or electricity. The RFS adopts the same approach for organic carbon in municipal solid waste that could be converted to a fuel. As Lee et al. (2017) point out, though, this treatment may be oversimplistic because, in part, the counterfactual scenario, or what would have happened to the waste if it were not converted toward further use as a fuel, chemical, or material, is not considered. Clearly, treatment of the waste gaseous carbon stream remains an area for examination. In any case, while the approach taken is subjective, consistency and transparency are essential if LCA results for carbon utilization processes are to be compared.

In addition to transparency in analysis assumptions, it is critical to use common—or at a minimum transparently documented—emission factors for key carbon utilization process inputs and inputs to the conventional fuels and products that the carbon utilization process is compared to (Artz et al., 2017). Otherwise, comparisons of LCA results are not meaningful. The table below contains emissions factors (GREET1_2017[1]) for the United States for the production of electricity

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[1] See https://greet.es.anl.gov/.

(national average grid) and hydrogen from several sources, which can enable consistent inputs into LCA of carbon utilization technologies.

TABLE 8-1 Emission factors for electricity and hydrogen.

Process Input	Emission Factor (GREET1_2017)
Gaseous hydrogen from different sources	
North American natural gas (NG)	0.11 kg CO_2e/MJ
Solar energy, nuclear energy	0.02 kg CO_2e/MJ
Electricity from different sources	
U.S. national average grid (34% coal, 32% natural gas, 20% nuclear, 4% residual oil, 10% other)	0.15 kg CO_2e/MJ
NG-fired power plant	0.14 kg CO_2e/MJ
Nuclear power plant	0.0025 kg CO_2e/MJ

Co-Products in LCA

In some cases, facilities converting waste gas emissions into products may have more than one output. As a simple example, a power plant with carbon utilization technology would produce both power and, potentially, a chemical or fuel. If the system boundary included the production of both power and carbon utilization–derived product(s), a technique to divide energy and emissions burdens among these products would be necessary.

Several different approaches to co-product handling are possible. Allocation approaches divide energy and emissions burdens among co-products based on their mass, energy, or market value shares. Von der Assen et al. (2013) considered a waste gaseous carbon utilization system that requires co-product allocation (Box 8-2, Figure 8-2). In this case, a power plant generates electricity co-producing a carbon utilization product, methanol. Here, the burdens of the system might be assigned between the electricity and methanol based on their market values. This approach is often considered relevant in systems in which one product drives the economic viability of the system producing the co-products. This can be the case for mining of platinum (Benavides et al., 2015), for example. Platinum is a high-value metal and recovering it is one of the main reasons why platinum mines operate, although the mass share of platinum is very small ($\sim 3 \times 10^{-4}$ wt%) among all metals produced at a platinum mine. A disadvantage associated with market allocation is that the market value of chemicals, fuels, and other products can fluctuate widely over time, which would cause LCA results to shift accordingly. Another option is to allocate system burdens based on the mass shares of the co-products. Mass allocation may be

relevant when a utilization technology produces more than one chemical product and the functional unit is on a mass basis. In the system considered in Figure 8-2, however, mass-based allocation cannot be used because electricity is massless. Finally, energy allocation is most applicable when all co-products are used for their energy content. For example, an analysis of the recovery of methane in biogas to displace natural gas use would likely use energy content to allocate burdens. Potentially, products emerging from a biorefinery using algae as a feedstock could be handled with energy allocation if they were mainly energy carriers, including a hydrocarbon fuel and potentially methane from anaerobic digestion of spent algae. However, not all energy content is functionally equivalent. Energy in the form of electricity is not functionally equivalent to energy produced by the combustion of a methanol fuel.

BOX 8-2

Co-product allocation in converting waste CO_2 from a power plant to methanol

When multiple products are derived from a system under analysis, it is often desired to calculate individual product LCA results (e.g., life-cycle greenhouse gas (GHG) emissions and water consumption), for example, to determine eligibility of single products in regulatory or certification programs (e.g., biofuels in the Renewable Fuel Standard). To do so requires a selection of a co-product allocation technique such as allocation by energy, mass, or market value. von der Assen et al. (2013) describe several options for handling co-product allocation for a system in which a power plant generates electricity and CO_2 that is converted to methanol.
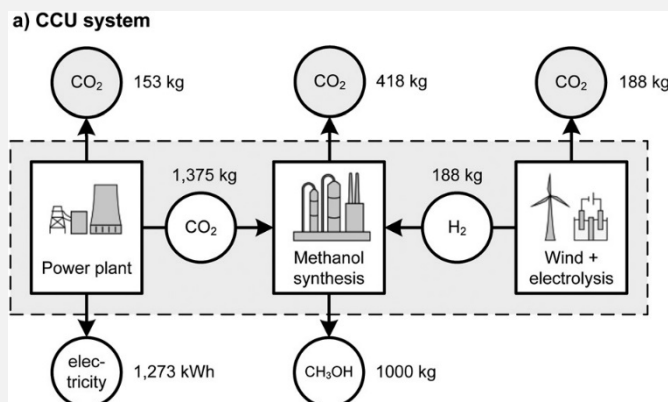
FIGURE 8-2 Flowchart and flow quantities (a) for the carbon capture and utilization (CCU) system producing electricity and methanol from CO_2, and (b) for the non-CCU reference system with traditional, non-CO_2-based technologies. CO_2 equivalent emissions for non-CCU methanol synthesis via steam reforming are taken from the ecoinvent database. CO_2 equivalent emissions for the coal power plants with and without CO_2 capture are taken from DOE. Republished with permission of RSC Publishing, from *Life-cycle assessment of carbon dioxide capture and utilization: Avoiding the pitfalls.* von der Assen, N., J. Jung, & A. Bardow. Energy & Environmental Science. 6. 2721-2734. 2013; permission conveyed through Copyright Clearance Center, Inc.

As the authors describe, one option is to allocate the power plant–associated burdens on the basis of the relative exergies (usable energies) of electricity and CO_2. Alternatively, the burdens can be allocated based on market considerations that treat the emitted CO_2 as a no-cost waste, a negative-value waste, or a positive-value co-product. The differing carbon intensity of CO_2 in each of these approaches leads to varying LCA results for electricity and methanol as displayed in Figure 8-3.
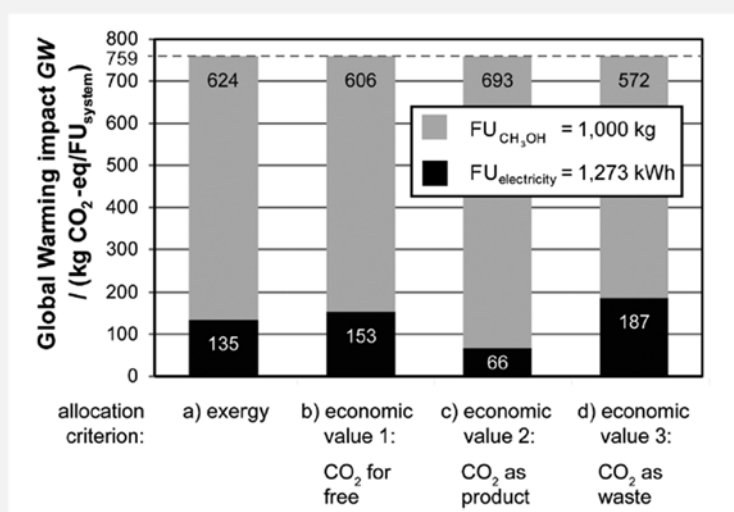
FIGURE 8-3 Allocated global warming impact (GW) values for electricity and for methanol as products from the CCU system in Figure 8-2. This analysis considers a functional unit of electricity to be 1,273 kWh and a functional unit of methanol to be 1,000 kg based on the system von der Assen et al. modeled. Republished with permission of RSC Publishing, from Life-cycle assessment of carbon dioxide capture and utilization: Avoiding the pitfalls. von der Assen, N., J. Jung, & A. Bardow. Energy & Environmental Science. 6. 2721-2734. 2013; permission conveyed through Copyright Clearance Center, Inc.

In this figure, electricity has lower life-cycle GHG emissions when CO_2 is treated as a product because methanol-bound CO_2 bears a greater share of power plant burdens. If CO_2 is treated as a negative-value waste, however, the electricity bears more of the burden and exhibits higher life-cycle GHG emissions. Correspondingly, the life-cycle GHG emissions of methanol in this case are lower than in any of the four cases von der Assen et al. (2013) consider. Transparency regarding co-product allocation method and rationale is very important to enable interpretation and comparison of carbon utilization LCA results.

In contrast to allocation techniques, which do not expand the system boundary, displacement or system expansion approaches do just that and take into account the displacement of conventional products. One common example of this approach is when corn-derived ethanol life-cycle assessments consider the displacement of conventional animal feed by biorefinery-produced distillers grains solubles (Canter et al., 2016). In this example, the corn ethanol is credited with avoided production of animal feed. It is important to note, however, that displacement credits are generally viable when applied to co-products that have a low share of total product output to avoid distorting LCA results (Wang et al., 2011). For example, in soybean-based production of biodiesel, glycerol is a co-product produced in the soybean crushing process: 82 percent of the mass output of that step is soy meal, and 18 percent is soy oil that is fed to the process stages that produce biodiesel. If the soy meal is treated as displacing animal feed and co-produced glycerol is treated as displacing petroleum-derived glycerol, life-cycle GHG emissions for soy biodiesel are approximately a third of the GHG emissions calculated with the market allocation method. Recently, Cai et al. (2018) examined co-product allocation methods for biorefineries co-producing fuels and chemicals. This is relevant to waste gaseous carbon systems that co-produce a fuel

(electricity or liquid fuel) and a chemical. They concluded that treating the co-produced chemicals as displacing conventional products is viable even if the mass share of the co-products is large. They note that if the market is not saturated with the co-produced chemical, displacement could be considered a viable approach. The authors also considered the process purpose co-product method, which examines the conversion process at an individual unit operation level and assigns burdens to products that "use" any given steps according to their mass, energy, or market value shares. This method requires unit operation-level material and energy flows from a facility or a process model and permits an in-depth analysis of which process burdens are attributable to which product. It is also possible to adopt a hybrid allocation approach, combining co-product treatments such as energy allocation and displacement, for example. Most critically, analysts should transparently report the co-product handling method they used and the rationale for doing so. If viable, investigating the sensitivity of results to co-product handling method should be reported.

Attributional and Consequential LCA

The techniques discussed in previous sections of this chapter would be adopted in attributional LCA, in which the supply chain of a product or process is followed linearly as a series of steps over which inputs and outputs are accumulated and assigned to the product of interest. As carbon utilization technologies achieve widespread market penetration, they will impact the structure of product markets. LCA modeling of the consequences of structural disruption through the economy, widely impacting material and energy consumption, is referred to as consequential LCA. This approach, most applicable when a disruptive as compared to an evolutionary change is expected, is adopted to capture indirect effects that would not be observed in a purely attributional approach. For example, CO_2 is used today as an input to carbonated beverage production, and the advancement of CO_2 capture and purification technology could influence the existing CO_2 market and shift how CO_2 is used. A detailed description of consequential LCA can be found elsewhere (Earles and Halog, 2011; Zamagni et al., 2012). To date, consequential LCA has been sparingly applied to waste carbon utilization and several outstanding research needs are apparent. First, many of the partial and general equilibrium models used in consequential LCA lack the detail necessary to track the influence of waste carbon–derived products, fuels, and materials on existing supply chains and markets. Development of more detailed models to represent these sectors is therefore a research need. Additionally, data sets used in consequential LCA may use outdated data which should be updated with recent chemical market information including production volumes and market prices. Furthermore, the treatment of uncertainty in consequential LCA needs to be further developed such that it is possible to better interpret consequential LCA results and discern the most significant drivers of environmental effects of disruptive use of waste carbon–derived fuels, chemicals, and products. Finally, there is a need to apply consequential LCA to waste carbon–derived fuels, materials, and chemicals that could be produced at volumes that are disruptive to current markets. It should be noted that, regardless of whether an attributional or consequential

LCA approach is adopted, uncertainty and variability are important to quantify to the extent possible (Igos, 2018; Lloyd and Ries, 2007). Uncertainty characterization may be difficult, however, in LCAs of waste carbon utilization given the emerging nature of the technology and limited data regarding conversion processes.

Temporal Issues

Carbon utilization product life cycles can extend over periods of months to decades and understanding the temporal distribution of emissions is important in comparing carbon utilization technologies. Some utilization technologies may delay CO_2 and/or CH_4 emissions for only a short period of time, while others may sequester carbon in products for decades or longer. In analyses that consider temporal factors, one key decision is the time horizon, or duration of study, that should be adopted.

As an example, if power plant CO_2 emissions are captured, treated, and converted to a polymer that is used in a durable plastic product, the pulse of CO_2 emissions from the power plant that would have occurred in year zero are reduced to some extent (taking into account emissions associated with the carbon utilization process itself) and the avoided emissions may be embedded in that durable product for decades, resulting in some degree of sequestration. If the durable plastic, however, were incinerated (rather than landfilled) after a useful life of just a few years, effective sequestration would be shorter.[2] Moreover, if the waste gas were converted to a chemical that would be used for several years in a process with some percent lost to process inefficiencies and/or combustion of process waste streams, effective sequestration would again be much shorter. Finally, if the waste gas were converted to a liquid fuel, any sequestration would be very short lived because the fuel would likely be combusted in a vehicle or at a power plant shortly after production. In other analyses with temporal aspects, for example, LCA of biofuels, time horizons including 30 years (for example, in the U.S. Environmental Protection Agency's Renewable Fuel Standard) and 100 years (Daystar et al., 2016; (Peters et al., 2011) have been adopted. Both Daystar et al. (2016 and Peters et al. (2011) offer insights into frameworks for incorporating temporal effects into LCA.

In all cases, it is important to consider what conventional fuels, chemicals, and products would be *displaced* as a result of the carbon utilization process. In the liquid fuels example, if the same energy content of fuel production from crude oil were avoided, less carbon from fuel combustion would be emitted on net with the utilization process serving essentially to accelerate the carbon cycle, taking CO_2 from a waste stream that was atmosphere bound, converting it to a fuel, and avoiding emissions of "fresh" CO_2 contained in fossil resources recently extracted.

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[2] Another possible end-of-life scenario for a plastic product or, potentially building materials, is recycling. If this is the approach the analysis adopts, concepts such as open- versus closed-loop recycling may need to be introduced. (See https://link.springer.com/content/pdf/10.1007%2FBF02978810.pdf. Accessed October 10, 2018).

Counterfactual Scenarios

In LCA, it is possible to consider counterfactual scenarios that account for what would happen if a new technology comes into use or a if a shift occurs in how technology is used. Then, emissions from the new technology case can be compared to the counterfactual, or business-as-usual, case to assess which scenario has lower emissions or impacts overall. Introducing a counterfactual scenario can be difficult because the evolution of technology and technology usage over time in both the new technology and the business-as-usual case must be projected, often with a significant uncertainty. For example, in an analysis of wood chip–derived power in the United Kingdom (Stephensen, 2014), counterfactual analyses considered what might happen to the land used to produce this biopower feedstock if the wood were not converted to chips for biopower. A number of counterfactual scenarios were included, ranging from allowing the land to become an old-growth forest to converting it to agricultural use. The choice of counterfactual scenario, which relied on essentially unknown future land management practices, greatly influenced results comparing biopower with conventional coal- or natural gas–derived power.

In the case of carbon utilization, a business-as-usual case would account for the fate of the waste gas and how a carbon utilization–derived product would conventionally be produced over time in the absence of carbon utilization technology. Furthermore, if it is assumed that renewable electricity or hydrogen is used in a carbon utilization process, it may be an element of a counterfactual scenario to evaluate other uses for these low–greenhouse gas process inputs (e.g., to fuel electric or fuel cell vehicles, or use in other processes).

The choice to incorporate a counterfactual scenario depends upon the intent of the analysis. If a carbon utilization LCA is intended to compare two different carbon utilization technologies to produce the same product, a counterfactual scenario may not be useful. If, however, the intent of the analysis is to consider using waste landfill gas to produce energy (Lee et al., 2017) or chemicals, it may be useful to consider over time how a business-as-usual scenario with ongoing landfill emissions compares to a new technology scenario with methane conversion to energy, or a product that may eventually be landfilled or incinerated.

RESEARCH AGENDA ITEMS

Compared to LCA of conventional fuels and chemicals, the field of carbon utilization LCA is developing and has specific challenges and considerations as described in the previous sections and Table 8-2. As the field evolves and LCAs of various waste gaseous carbon utilization technologies grow in number and complexity, it will be critical for analysts to consider and document their approach to transparently reporting their data, data sources, and assumptions.

TABLE 8-2 Summary of key LCA considerations for different types of CO_2 utilization products.

	Building Materials	Polymers	Chemicals	Liquid Fuels
System Boundary	• CO_2 source and purification, compression, transportation steps • Sources of hydrogen and electricity • Development of analogous system boundary for comparison system • End-of-life, whether combustion, incineration, disposal, or recycling should be included • For long-lived products (e.g., polymers that do not degrade) their end of life should be noted as outside the system boundary if the analysis time horizon does not incorporate their degradation			
Functional Units	• CO_2 emitted over material lifetime per unit mass • CO_2 abated compared to a reference system	• Direct displacement: per kilogram product • Functional displacement: per unit mass required for equivalent performance		• Per unit energy
Co-products	• Limited co-products	Treatment options include • Displacement • Energy • Mass • Market value		• Energy products could be treated with energy allocation • Other co-product options are identical to those for chemicals and polymers
Temporal	• Long-term storage likely although consideration of product lifetime compared to conventional products warranted • Choice of time horizon will determine whether waste carbon effectively sequestered for long-lived products		• Waste carbon storage duration dependent upon chemical application • Processes such as evaporation or decomposition (or incineration of waste chemicals) could lead to the carbon in the chemical being emitted to the atmosphere	• Essentially no storage of waste carbon • Carbon in fuel emitted to atmosphere upon combustion
Attributional & Consequential LCA	• Intent of analysis drives LCA approach • Comparison of nearly identical systems or evaluation of nondisruptive systems may be suitable for attributional LCA • Evaluation of disruptive technology changes may be suitable for consequential LCA			
Potential Counterfactual Scenarios	Building materials such as wood, steel, or aggregate that do not incorporate waste CO_2	Ongoing widespread use of fossil fuel–derived polymers or some level of penetration of biomass-derived polymers	Alternative emerging technologies (e.g., new feedstock from biomass, new catalysts, new separation technologies)	Electricity or fossil- or biomass-derived liquid fuels or a combination thereof

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In addition to the issues identified earlier in this chapter, there remain outstanding needs and issues associated with carbon utilization LCA for analysts to investigate and resolve:

- What is the best way to evaluate carbon utilization pathways that are emerging in the absence of large-scale production data and how frequently should the analysis be updated as the technology develops?
- What is a defensible technique to capture uncertainty in carbon utilization LCA results given the emerging nature of the technology?
- What are standard baselines that can be employed as business-as-usual cases for counterfactual analyses?
- Which system boundary assumptions and decisions are defensible for analyses that target different questions?
- When is it appropriate to introduce consequential LCA and what methods represent best practice?

Overall, the committee identified priority research needs to address the issues raised in this chapter. Priority areas include the following:

Life-cycle assessment benchmarking

Research is needed to develop benchmark life-cycle assessments of waste gas generation, waste gas cleanup, waste gas transport, electricity inputs, hydrogen inputs, and other enabling technologies to facilitate consistent and transparent assessments of the net greenhouse gas emissions of carbon utilization technologies. These benchmark assessments should include multiple environmental attributes of carbon utilization life cycles, such as greenhouse gas emissions, water use, air emissions, and materials use. This could lead to more consistent assessments of technologies.

Life-cycle assessment of emerging waste carbon utilization technologies

Research is needed to learn from transparent life-cycle assessments of emerging technologies, taking into account a system boundary that includes waste gas capture and cleanup, the conversion process, the use phase, and end-of-life considerations. Although LCA results for emerging technologies will undoubtedly evolve, LCA at this early stage will help guide research toward activities that will heighten energy and environmental benefits.

Assessment of disruptive change

Research is needed to develop life-cycle assessment tools that move beyond assessing marginal changes in existing, static systems and address disruptive changes resulting from large-scale carbon utilization. This will provide tools for assessing disruptive changes necessary for performing consequential LCAs of CCU systems.

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9

Assessing Commercial Viability of Carbon Utilization Technologies

INTRODUCTION

A number of technologies for transforming gaseous carbon wastes into useful products are being explored, and although some of the technologies have reached the commercial stage (Zimmerman and Kant, 2015), the majority are still in various stages of research and development. Assessing the commercial viability of carbon utilization technologies enables the comparison of technologies and the identification of areas where research and development might be most impactful. The evaluation of the commercialization of potential carbon utilization products or processes requires consideration of technology and economic viability, which are traditionally determined by conducting technoeconomic analysis (TEA), as well as other factors which may or may not be part of a TEA, as depicted in Figure 9-1, including strategic fit with a company's long-term goals, global standards, and intellectual property (Lee et al., 2017).
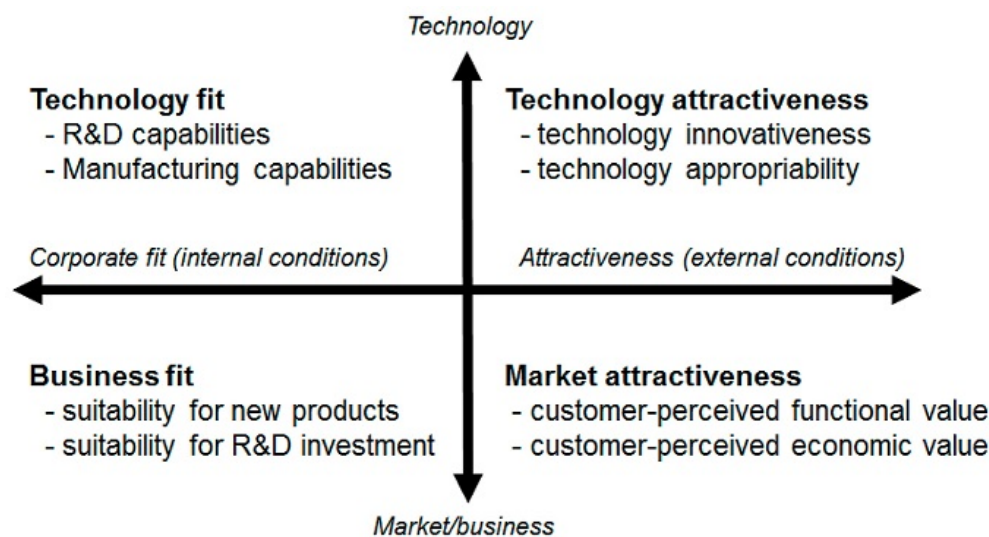
FIGURE 9-1 Criteria often utilized in commercialization decisions. SOURCE: Lee et al., 2017.

A variety of strategies have been developed to systematically assess all types of commercialization viability. Several years ago, researchers at the University of Cincinnati proposed a method for systematically evaluating commercialization potential, which they called

the Strategic Technology Evaluation Program (see Figure 9-2), or STEP (Bandarian, 2007). While this is not the only framework for technology evaluation, the committee used the STEP framework in its evaluation of carbon utilization. The application of the STEP framework to assessing the commercial potential of carbon utilization begins with the technology area, shown on the far left of Figure 9-2.

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                        ┌──────────────┐
                        │  Commercial  │
                        │  Potential   │
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        ┌──────────────────────┼──────────────────────┐
  ┌───────────┐          ┌───────────┐          ┌───────────┐
  │ Technology │          │  Market   │          │   Legal   │
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│Evaluation││Evaluation││Evaluation││Evaluation││Evaluation││  Policy  │
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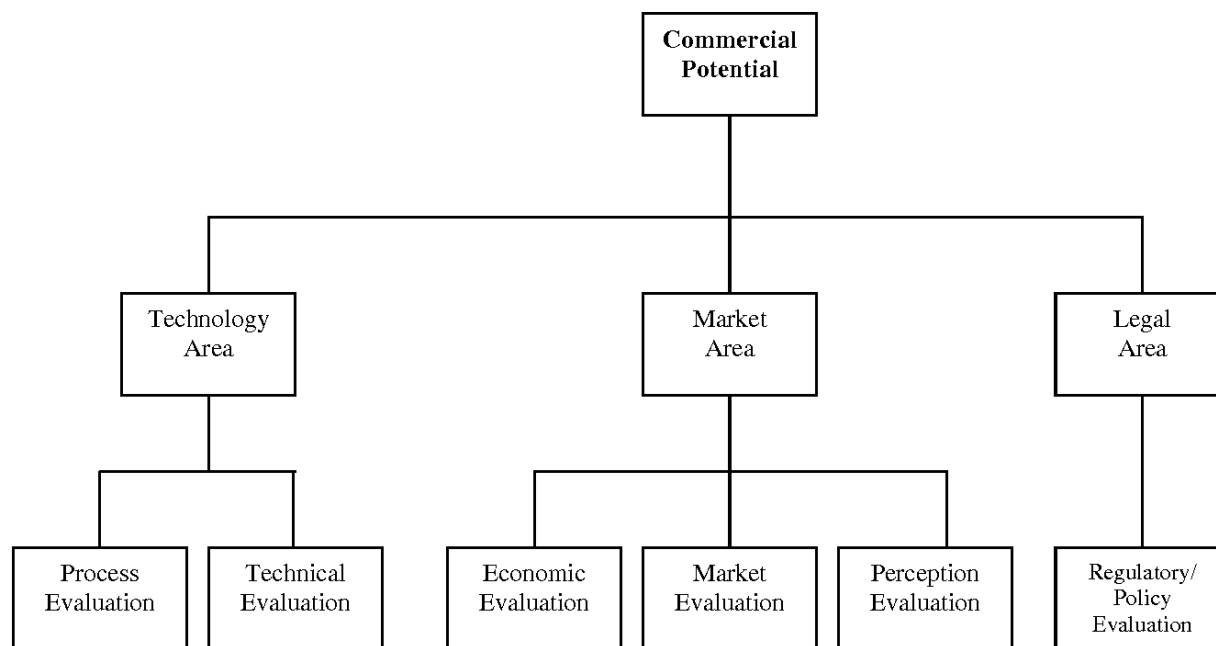
FIGURE 9-2 The Strategic Technology Evaluation Program, STEP, was developed to systematically assess commercial potential for new technologies. SOURCE: Bandarian, 2007

ASSESSMENT OF THE TECHNOLOGY AREA

Technoeconomic Analysis

Technoeconomic analysis is a tool that is widely used to evaluate commercial viability of any new technology. TEAs are applied at multiple stages of the research and development process, with the information required, and the assessment methodology and rigor utilized become more detailed as the technology advances. The starting point for a TEA is to lay out a conceptual process design. Initial inputs may come from literature references, thermodynamic and process modeling, or scoping experiments. As technology development advances (see Box 9-1), engineering optimization will identify the major technical hurdles as well as the theoretical process yields based on thermodynamics. At this point, if the economics are still favorable, more detailed process flow diagrams will be developed so that engineering simulations can begin. The conceptual process

description will outline all of the unit operations (e.g., pretreatment, reactor, separation, purification, recycle, etc.). Once the process flow is better defined, material and energy balance models are developed to assess the technology.

For the various technology readiness levels described in Box 9-1, TEAs can be performed and used to set technology improvement targets. At the fundamental research scale, relatively simple approaches involving values of reactants and products can be employed. These models can be the basis of cost estimations that can set targets for technology improvements. For example, a TEA for converting CO_2 captured from a coal-based power plant to methanol concluded the process could only be economically attractive if the market price of methanol doubled, the cost of H_2 was reduced by 250 percent, or the CO_2 feedstock was highly valued (222 €/ton in 2015) (Pérez-Fortes et al., 2016). For pilot and higher levels of development, more detailed information regarding materials of construction, process control criteria, as well as expected equipment lifetimes will feed into further economic analysis and target setting.

Generally, for comparison of multiple technologies to solve a unique problem like CO_2 management, a common costing framework is developed for use at various maturity levels. An example of a costing framework is described by Rubin et al. (2013) for CO_2 capture technologies, which have been under development since 1995. Utilization of gaseous carbon waste streams is relatively a new technical area and most of the technologies are at a very early stage of development (Technology Readiness Levels (TRLs) 1-3) and thus not many engineering or process development insights have been developed. Therefore, development of a common costing framework for carbon utilization technologies will happen as technology maturity advances.

In general, the economics of renewable H_2 make many of the CO_2 utilization strategies uncompetitive with traditional technologies even though CO_2 is a waste product. Currently only fossil-derived H_2 can meet the Department of Energy's target of supplying H_2 at less than \$2/kg expressed in 2007 dollars, with electrolysis-based methods being nearly threefold higher in cost (HPTT Roadmap, 2017). Because the economics can be challenging, initiatives to subsidize demonstration plants such as the EU Innovation fund are being proposed to accelerate technology development.[1] In the United States, the 45Q Tax Credits (as explained in detail later in this chapter) to fossil energy users to sequester or reuse their CO_2 emissions is also intended to encourage industrial investments in these technologies (Silverstein, 2018).

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[1] https://ec.europa.eu/clima/news/public-consultation-establishment-eu-innovation-fund_en (accessed October 10, 2018).

Box 9-1

Technology Readiness Levels

Technology readiness levels (TRLs) are a method of estimating technology maturity. TRLs are used by a number of funding agencies including the U.S. Department of Energy to define the stage of technology development for a given application. For simplicity, the technology development process can be described by the successive steps in the right-hand column of Table 9-1, which are used to describe the state of the technologies considered throughout the report.

TABLE 9-1 Description of the technology readiness levels.

Technology Readiness Level (TRL)		Stage of Development
TRL 1	Fundamental principles observed and reported	**Fundamental Research** (concept formulation, laboratory-scale proof-of-concept testing, initial modeling)
TRL 2	Technology concept and/or application formulated	
TRL 3	Analytical and experimental critical function and/or characteristic proof of concept	
TRL 4	Component and/or system validation in laboratory environment	**Bench Scale** (testing to obtain initial engineering data)
TRL 5	Laboratory scale, similar system validation in relevant environment	
TRL 6	Engineering/pilot scale, similar (prototypical) systems validation in relevant environment	**Pilot** (developing a small prototype and doing integrated testing)
TRL 7	Full scale, similar (prototypical) system demonstrated in a relevant environment	**Demonstration** (design, building, and operating a reasonable size unit where key technology risks can be addressed and mitigated)
TRL 8	Actual system completed and qualified through test and demonstration	**Commercial–limited** (stage of commercialization where a product is manufactured in an area with specific advantages that make it viable due to the local environment, regulatory, or other factors)
TRL 9	Actual system operated over the full range of expected conditions	**Commercial–broad** (stage of commercialization where a product is manufactured in such a way that it does not rely on local environment, regulatory, or other factors)

Technical/Economic Factors Relevant to Carbon Utilization

The TEA methodology described above is generally applicable; however, in assessing technologies for utilization of gaseous carbon waste streams, particular attention has to be paid to the following technical and economic factors:

1. Cost, quantity, and purity of the gaseous carbon waste stream available;
2. Cost and carbon footprint of other reactants (as described in detail in Chapter 8 on LCA), in particular if H_2 for reacting the waste gas to make products is needed;
3. Cost of utilities, in particular electricity and steam (and their carbon footprint per LCA guidelines);
4. Quality of the product made and its marketability at desired price;
5. Boundary conditions or battery limits for process technology: inside battery limits versus outside battery limits;
6. Availability of capital with appropriate risk tolerance; and
7. Policy drivers (e.g., tax credits, subsidies, green premium, and preferred markets).

Insights provided by TEAs for early stage carbon utilization technologies are illustrated by the following examples.

Example 1: CO$_2$ Capture from Power Plants

A first example of a TEA considers capture of CO_2 from coal- and natural gas–fired power plants to develop a research and development roadmap for CO_2 capture technologies. A comprehensive study done by the National Energy Technology Laboratory (NETL) in 2015 has been used as a benchmark to track the progress of Department of Energy Fossil Energy Research and Development (R&D) in the CO_2 capture domain (NETL, 2015). This study was performed using consistent and transparent methodology (all the assumptions were carefully documented), and it established performance and cost data for fossil energy power systems, including pulverized coal (PC) plants fueled with bituminous coal and natural gas combined cycle (NGCC) plants, all with and without carbon capture and storage. The cost and performance data used in this study were compiled from published reports, information obtained from vendor quotes and users of the technology, and data from designing and building electric utility projects. The study found that adding CO_2 capture was the largest component of the cost of electricity for PC (75 percent) and NGCC (52 percent) and adds between \$56/ton of CO_2 captured for PC and \$71/ton of CO_2 captured for NGCC. Sale of the captured CO_2 for utilization applications could provide a revenue stream to improve the economics of carbon capture; however, if the full cost of carbon dioxide capture is applied as a CO_2 feedstock price to utilization technologies, the feedstock price will be of order \$60 per ton of carbon dioxide with current technologies. However, as the carbon capture technologies mature, the carbon capture cost from combustion facilities is expected to come down.

Example 2: Production of Methanol and Fuels from CO_2

As discussed in Chapter 4, Carbon Recycling International in Iceland produces approximately 4,000 tons of methanol from CO_2 each year using the renewable hydro and geothermal energy to produce H_2 via electrolysis and uses CO_2 captured from a geothermal power plant located next to the CO_2-to-methanol facility. Simple calculations based on the reaction stoichiometry of $CO_2 + 3\ H_2 = CH_3OH + H_2O$ indicate that if the H_2 price from renewable energy is \$4/kg, and CO_2 (of desired purity and concentration needed for this reaction) is free similar to the Iceland case, the contribution of H_2 itself to the methanol cost will be about \$750/ton (compared to a conventional methanol cost of approximately \$423/ton),[2] assuming no capital and operating costs. If the H_2 price comes down to about \$2/kg from renewable electricity, this cost will reduce to \$375/ton of methanol. Under this scenario, methanol produced from waste CO_2 may become cost competitive. This high-level TEA provides useful insights on where to focus research and development efforts.

Example 3: Biogas Conversion

As discussed in Chapter 7, effective conversion of biogas into value-added products requires biogas upgrading to remove CO_2 and other contaminants (H_2S, siloxanes, HCl, H_2O, etc.). Some biogas can contain as much as 50 percent CO_2 as discussed in Chapter 7. Biogas upgrading processes are quite capital intensive and, as a result, methane produced from biogas cannot generally compete with fossil methane. However, biogas plants are being built worldwide with government incentives to produce a number of products. Besides electric power and heat, other products include bio-CNG (compressed natural gas), bio-LNG (liquefied natural gas), bio-H_2, and bio-CH_4 to produce chemicals and fuels. The Environmental Protection Agency classifies biomethane as renewable natural gas (RNG). The RNG qualifies for the credits promulgated for Renewable Fuel Standards through Renewable Index Numbers (RINs). For example, \$1/gallon RIN credit (based on ethanol price) will add about \$7 per million British Thermal Units (MMBtu) premium to biomethane. This premium is encouraging private-sector investment in biogas plants.

Sensitivity Analysis

Sensitivity analyses of TEAs for the evaluation of early stage carbon utilization technologies can often reveal key research needs. The results of such sensitivity analyses are often shown in "tornado charts." The committee was not able to identify any public domain comprehensive TEA sensitivity analysis for commercial technologies; however, a recent technology development example with flared natural gas conversion to methanol can be used as an illustration for future CO_2 utilization processes. An example of a tornado chart for the flared gas conversion is shown in Figure 9-3, which shows a sensitivity analysis of a novel technology

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[2] See https://www.methanol.org/news/methanol-price-trend-overview-forecast-2018/.

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being developed by RTI International and Massachusetts Institute of Technology to convert flared gas into methanol using an engine reformer (Browne, 2016). In this process, methane is partially oxidized with air into syngas in a commercial internal combustion engine operating in a fuel-rich mode. The resulting syngas is cleaned and conditioned using traditional methods to produce a syngas with a H_2-to-CO ratio of 2 to feed into a catalytic reactor to produce methanol. From Figure 9-3, the capital cost of the system emerges as the most important factor. In the figure, a baseline capital cost estimate of $1.43 million was used, while a 50 percent change to the capital cost was used as upper and lower bound. The figure shows that a 50 percent reduction in capital cost reduces the methanol production cost by approximately $0.20/gallon. This suggests that research aimed at reducing capital costs, especially of the compressor or the need for compression, is a high-priority target. This is an example of using sensitivity analyses of TEA to identify priority research areas when developing new technologies for utilization of gaseous carbon wastes. Sensitivity analyses are employed not only to identify research targets, but also to understand the impact that key assumptions have on TEAs. The sensitivity analysis also provides a good window on cost and performance to account for variability and uncertainty associated with early stage development of the carbon reuse technologies. For example, project and process contingencies can be incorporated in the sensitivity analysis. The value of these contingencies will depend on the maturity of the technology (AACE, 1991).
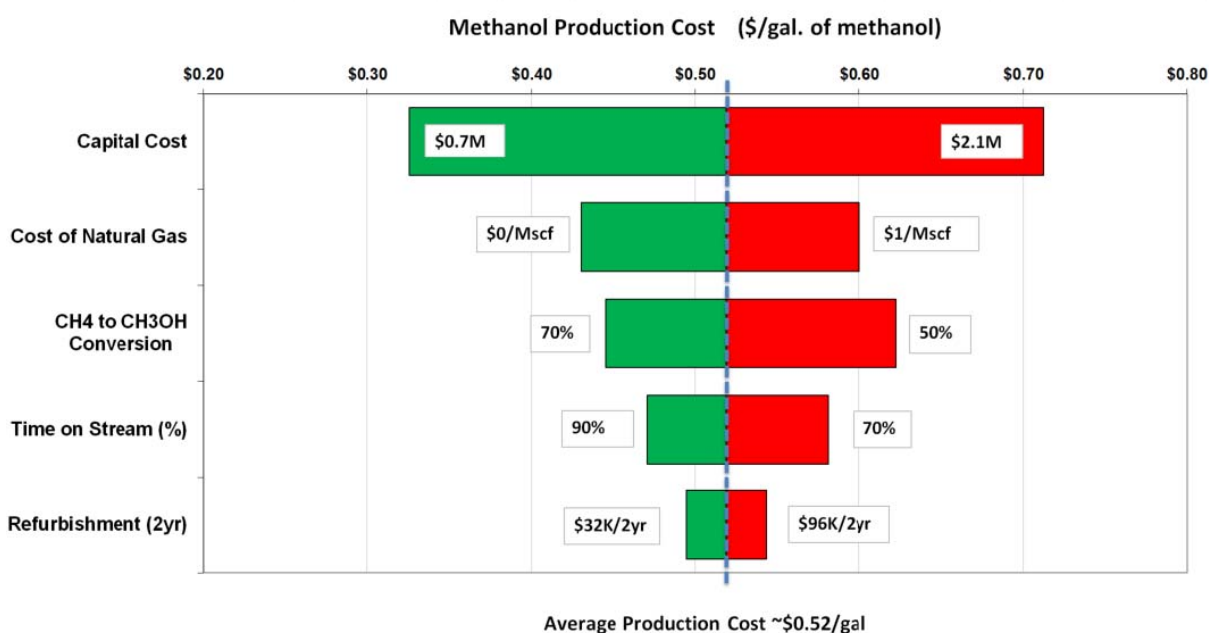
FIGURE 9-3 Sample tornado chart for the production of methanol from methane using an internal combustion engine as a reactor. The bars illustrate different methanol production costs in response to different assumptions for capital cost, cost of natural gas, conversion rate of methane to methanol, time on steam, and refurbishment cost. SOURCE: Browne, 2016.

The sensitivity analysis can be extended to estimate costs of a first-of-a-kind (FOAK) plant and extrapolate it to the Nth-of-a-kind (NOAK) plant. FOAK cost estimations are generally made for a first commercial plant based on a new technology built with the maximum amount of standard equipment and materials, and labor and productivity assumptions based on recent design and operational experience and lessons learned with similar plants. FOAK plants are typically designed conservatively with redundancies to minimize unanticipated operational risks. In most cases, FOAK plant cost represents the highest capital cost per unit of product volume. With building of multiple plants, a technology learning curve is used to develop the cost estimates of a NOAK plant (NETL, 2013). Depending upon the maturity and market penetration of the technology, the cost of a NOAK plant can be 10-50 percent lower than a FOAK plant cost. Other contributing factors are scale, modularity, materials cost, inflation, geographic location, and regulatory compliance. For the CO_2 utilization technologies, it is expected that NOAK plant costs could be 10-25 percent lower than a FOAK plant based on a NETL study (NETL, 2013).

ASSESSMENT OF THE MARKET AREA

Moving past the technology assessment, the next step in commercialization assessments is to assess the market area. A key feature of the market area leg of STEP is the definition of the market a particular product or technology will be able to address (Jain et al., 2003).

With a new technology, there needs to be a full understanding of the market opportunities. Interviews with potential customers are often utilized to better understand the market needs and to determine whether the new technology offering will be unique. These interviews can be part of an iterative process as the technology continues to be better defined as it develops. A successful application of TEA combined with interviews was documented in a recent report on graphene oxide membrane development (Dave, 2017). After using TEA to determine their graphene oxide membranes were not economical for reverse osmosis applications, researchers used industrial interviews to identify opportunities where there were unmet needs. As shown in Figure 9-4, three areas of unmet needs included mass-market polymer membranes, emerging solvent-resistant membranes, and high-temperature polymer membranes. The yellow dot in Figure 9-4 illustrates the current focus of the science community among the other unmet needs. The results of the TEA opened up entirely new scientific areas to explore (Dave, 2017).

Because carbon utilization technologies are largely early in their development, detailed customer interviews are not possible. However, initial feedback from customers has been favorable for CO_2-based products, especially if the incorporation was longer lived and if the fossil resource savings were viewed as being meaningful. Interestingly, the amount of CO_2 incorporation in the product was not a significant factor for consumer preference (van Heek et al., 2017).
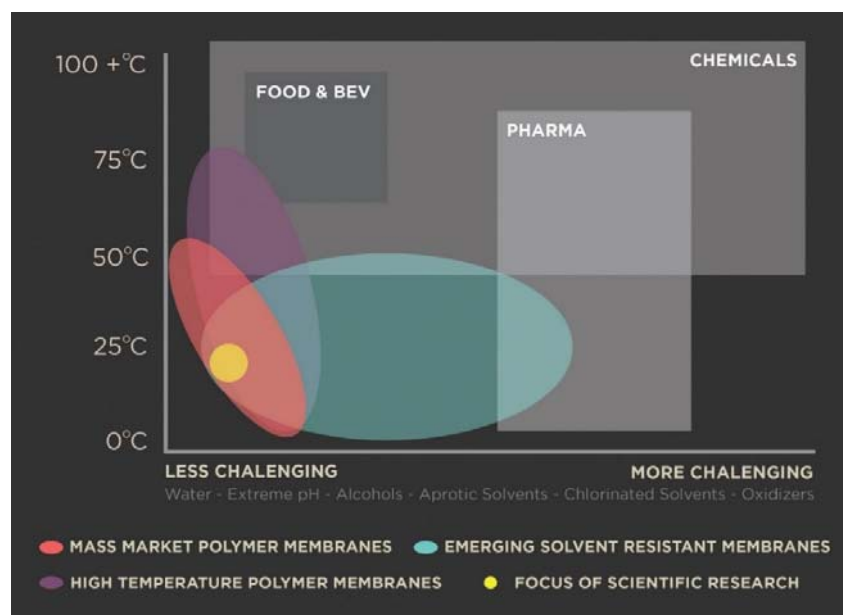
FIGURE 9-4 The ovals represent the specified operating conditions of commercial nanofiltration membranes today. The boxes illustrate the desires of industrial process separations, based on nearly 200 customer interviews. There is a mismatch between what is available and what is desired, and yet the bulk of academic research is focused on the yellow dot.[3]

Factors to Consider for Market Evaluation

Differentiating Aspects to New Technologies

An assessment of the differentiation advantages of a new product can be difficult and often requires having detailed market understanding. For example, when products based on compostable biobased polylactic acid were first introduced into the market, they were not well received, either by consumers because of changes in the performance or by manufacturers because they required changes in downstream manufacturing. In addition, while the polymer had environmental advantages, it was also more expensive to manufacture, making market adoption difficult (Iles and Martin, 2013). In general, consumers are not willing to pay a premium for a "green" product. However, Braskem's bioethanol-based polyethylene (PE) is an example where through new business models, they were able to define a 15-30 percent "green" premium over traditional PE via development of the "I am Green" product label based on the ASTM D6866-11 international standard for determining the biobased content via radiocarbon analysis. In this case, the offering is identical to more traditional feedstock-based PE, so there are no needed changes in downstream manufacturing, removing this hurdle from introducing the technology (Iles and Martin, 2013).[4]

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[3] Reprinted from *Six Degrees of Separation: Connecting Research with Users and Cost Analysis,* Joule 1, 410-415, Dave, S. H., B. D. Keller, K. Golmer, & J. C. Grossman, Nov. 15, 2017, with permission from Elsevier.
[4] See https://www.iccsafe.org/.

Because preliminary consumer interviews do not suggest a preference for higher CO_2 incorporation, it is unclear whether establishing a similar market preference will be possible in gaseous waste carbon–derived products (van Heek et al., 2017).

Potential Market Barriers for New Technologies

While the majority of market evaluation focuses on the end market for the technology, an equally important factor is to identify any potential barriers leading to the end market to understand if there will be changeover costs for introducing a new technology. An example illustrating some of these issues is in the introduction of polyvinyl chloride (PVC) into the North American marketplace. While it was first introduced in limited applications in 1952, it could not penetrate into the housing market until the mid to late 1960s, despite its advantages and demonstrated durability. The delay was in part due to necessary changes to building codes. As highlighted in Figure 9-5, market penetration of PVC increased rapidly after it was accepted into various building codes. However, a switch to PVC pipe would also result in lost revenue for plumbers and pipe distributors, and their concerns helped to slow the market expansion of PVC as is also depicted in Figure 9-5 (Boren et al., 2012; Musso, 2009). Assessment and management of displacement concerns will be a key step toward introducing new feedstock-based products into the market place.
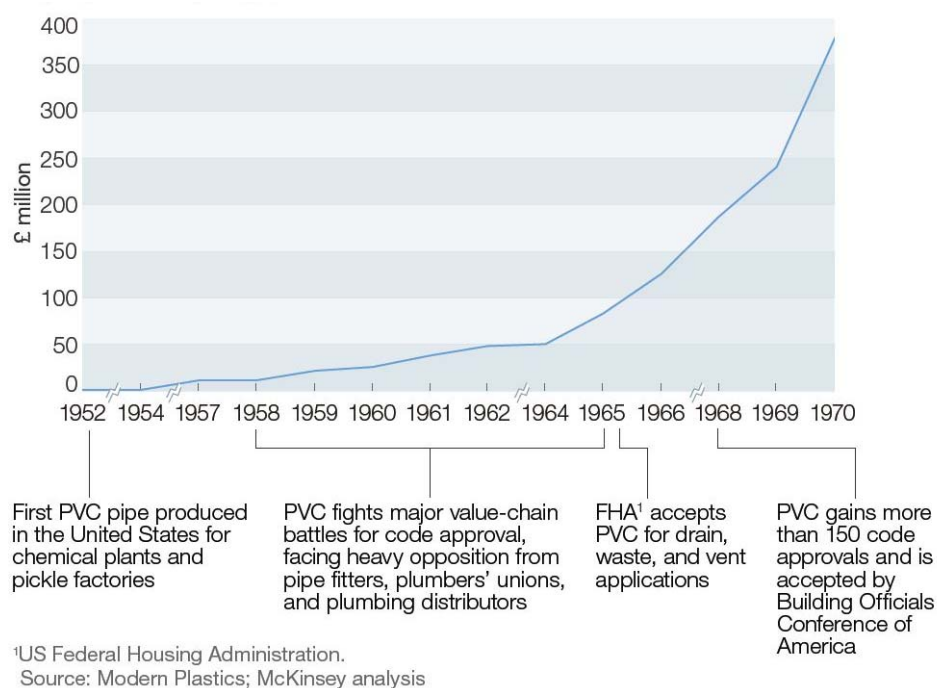
FIGURE 9-5 North American market penetration of PVC pipeline. Exhibit from "The path to improved returns in materials commercialization", 2012, McKinsey & Company, www.mckinsey.com. Copyright (c) 2018 McKinsey & Company. All rights reserved. Reprinted by permission.

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Perception Evaluation

Perception evaluation is tied with the market evaluation, yet it can impact more than the addressable market. Perception evaluation is subjective and can be geographically and/or demographically centered. For example, the willingness of a consumer to purchase products made from waste materials or prepared using genetically modified organisms could differ dramatically depending upon the location of the market (Jain et al., 2003). Perception issues provide barriers to commercialization (Kant, 2017). Providing consumers with access to accurate information can be a barrier (Jones et al., 2017). For example, a recent study with "mystery shoppers" demonstrated car dealerships themselves were negatively affecting electric vehicle sales due in part to a lack of knowledge of the technology as well as a lack of willingness to promote the technology due to their perceptions about viability and profitability of electric vehicles to their dealership (de Rubens et al., 2018). As many of the gaseous waste carbon–based products like chemicals are intermediates which will not be immediately marketed to the public, many of the current educational efforts are aimed at the business level and not at the final consumer. It is unclear how the resulting products made from these intermediates will ultimately be marketed (Jones et al., 2017). Overall, the adoption of products derived from gaseous carbon waste streams could similarly be challenging without an understanding of consumer perceptions. Engaging behavioral economists could be helpful in conducting perception evaluations to ensure the assessment is robust to minimize risk.

ASSESSMENT OF THE LEGAL AREA

The last branch of STEP (see Figure 9-2) is the legal branch. Like perception evaluation, policy and regulatory evaluation could be highly regionalized. In dealing with the gaseous carbon waste streams, this evaluation leg will be particularly important to fully assess the serviceable addressable market[5] as well as the economics of the technology.

Policy Evaluation

The geographical concentration of CO_2 utilization efforts has been found to mirror the availability of public funding, which was the main driver for the development of these technologies rather than a market pull (Kant, 2017; Zimmermann and Kant, 2017). If subsidies or other policies are in place that can improve the new technology's competitiveness, it is also important to understand their longevity to determine the impact on investment returns. If these subsidies or

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[5] The total addressable market is the revenue opportunity for a product or service if 100 percent of the market share was achieved, whereas the serviceable addressable market is the portion to the total addressable market which can be serviced by a given product or service.

policies are well defined, they can be incorporated in the TEA. An example is the recent legislation passed by Congress in March 2018 (Futures Act): beneficial reuse of CO_2 to produce products such as fuels, chemicals, plastics, and construction materials such as cement, or to produce algae to make biofuels will qualify for a tax credit starting from $12.83 per ton of CO_2 and linearly increasing to $35 per ton by 2026 and thereafter adjusted every year for inflation. The legislation requires a minimum of 25,000 tons of CO_2 use and tax credits are valid up to 500,000 tons of CO_2 per plant. Besides capturing and utilizing CO_2 from coal- and natural gas–fired power plants, the tax credits under 45Q are valid for utilizing CO_2 produced from ethanol, ammonia, hydrogen, natural gas sweetening, and other industrial sources.[6]

Regulatory Evaluation

Regulatory issues could either improve the chances that a technology is adopted or prove problematic for developing carbon utilization technologies. For example, regulations that impact the price of gaseous carbon emissions would change the economics of carbon utilization technologies. Building codes or other regulations could influence the adoption of technologies such as CO_2-enhanced concrete, requiring extensive testing and verification. Interviews with CO_2 utilization ventures found that many of them were concerned about the regulatory context, citing that regulations are based on current technologies and may exclude new technologies (Kant, 2017). For areas like construction materials or consumer goods, these could be significant hurdles for new gaseous carbon waste–containing products. The complexity of this issue was discussed in Chapter 3, where construction standards and codes may vary across small geographical areas, for example, city-specific codes. In these cases, a significant amount of resources will be spent in application testing and verification rather than in development of the technology itself. Further complications for introducing new products arise when the products need to be tailored for individual market segments. Therefore, linking early stage technologies with companies familiar with the end consumers is very important (Maine and Seegopaul, 2016). Regulations are not harmonized so global introduction of new technologies could be problematic (Kant, 2017).

Intellectual Property

An evaluation of intellectual property (IP) associated with the technology is also an important part of the legal evaluation. There are two perspectives that can be used for IP evaluation: (1) freedom to operate and (2) strength of the IP. Freedom-to-operate analysis identifies blocking patents which need to be licensed to practice the technology and/or for any potential infringement issues. Lack of clarity on the IP is a barrier to investment in the development

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[6] See https://www.forbes.com/sites/kensilverstein/2018/02/15/tax-credit-may-rev-up-carbon-capture-and-sequestration-technology/#4e0a53774a06.

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and commercialization of the technology. Having an IP strategy in place is also necessary for facilitating customer interactions (Kant, 2017). Good decisions around what to disclose and what to maintain as expertise and trade secrets can also be key to deterring competition as well as securing licensing for a new technology (Arora, 1997).

OVERALL COMMERCIALIZATION CONCLUSIONS

In the preceding sections, factors in three areas—technology, market, and legal—were described for evaluating commercial viability. However, even if all of these criteria are met, the resulting technology may still not be a commercial success. Through a series of interviews and analysis of successful innovations in the chemical industry, McKinsey outlined the challenges in the market introduction of technology (Miremadi et al., 2013). A high-level summary of their findings is presented graphically in Figure 9-6.
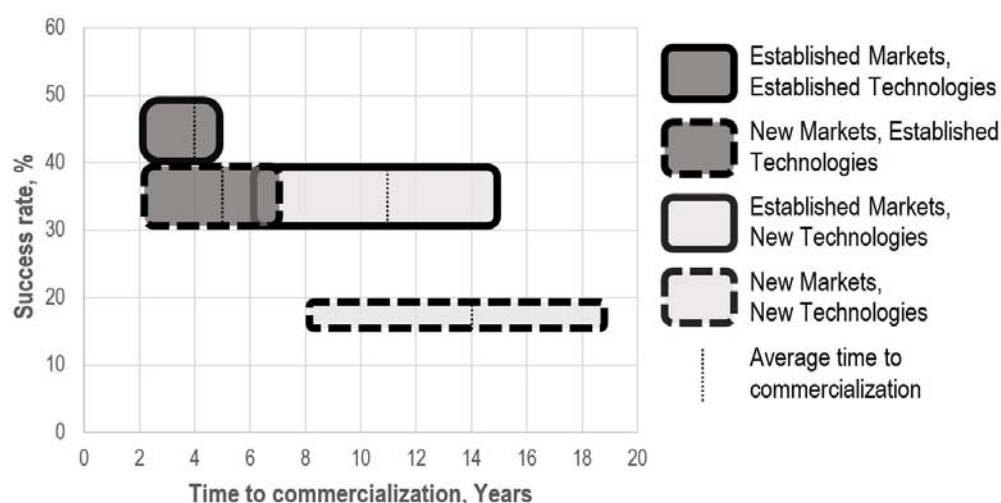
FIGURE 9-6 Analysis of new chemical innovations based on results summarized by Miremadi et al. (2013). In this diagram, the outlines of the bars designate the range of commercialization times and success rates seen for chemical products in these categories and the dotted lines depict the average commercialization time for each category.

In this summary, commercialization time is defined as the length of time from the project launch to the point where the annual sales are equivalent to the R&D investment, and the success rate is defined as the percentage of projects with positive return on a net present value basis, using the cost of capital with no risk adjustment. The study identified the interaction between two factors, the "degree of market familiarity" and the "degree of technology familiarity," to bin the time to commercialization and success rates. In the best-case scenario (high degree of market familiarity

and high degree of technology familiarity), the commercialization time for established markets ranged from 2 to 5 years with a success rate ranging from 40 to 50 percent. For these products, the development costs were typically lower than for other types of products, and as a result, the margin, the gain associated with the new product as compared with the product it replaced, above any market cannibalization,[7] is only 0-5 percent. In contrast (low degree of familiarity and low degree of technology familiarity), product introductions of a new technology into a new market are far more complex, with commercialization times ranging from 8 to 19 years and success rates of 15-20 percent. Because these are new technologies, the majority of the commercialization time is spent on technology development, yet the reason many of these technologies fail is because of poor definition of new markets (Miremadi et al., 2013).

Many of the strategies for gaseous carbon waste utilization are based on developing "drop-in" technologies for established markets. For the chemical industry, the McKinsey assessment would predict a 30-40 percent success rate for this approach with timelines on the order of 6 to 15 years to allow for full evaluation and vetting of a new technology as companies will be very hesitant to harm their reputation by launching a new technology into one of their well-established markets (Miremadi et al., 2013). Because waste gas streams may contain variable trace components, additional evaluation may be necessary in order to validate full qualification for a particular application.

RESEARCH AGENDA ITEMS

As discussed throughout this chapter, evaluation of the commercial potential for new technologies is complex as more than just the technology needs to be factored into the assessment. These problems are multifaceted and, as such, a multidisciplined approach will be needed for successful technology product launches based on these new feedstocks. Understanding of market and societal implications of introducing new technologies will help in identifying market opportunities for new technologies and in identifying communication strategies to educate consumers and the marketplace on the societal value of developing and using these products. The development of databases of technical performance, financials, and cost of various CO_2 utilization technologies at different stages of maturity will support the development of knowledge-sharing networks. Additionally, development of predictive and analytic tools for detecting consumer trends and tools for identifying suitable production locations based on inputs such as raw material availability and/or suitability, favorable permitting requirements, and so on would improve technology development and commercial deployment. Ideally, collecting feedback from potential industrial users and consumers throughout the research process could both accelerate progress and increase the likelihood of commercial success. The committee identified priority research needs to consider when conducting TEAs for carbon utilization:

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[7]A reduction in sales volume or sales revenue of a product as a result of the introduction of a new product by the same producer.

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Technoeconomic assessment benchmarking

Research is needed to develop standardized, transparent inputs and assumptions for technoeconomic analysis implemented for carbon utilization. This could lead to more consistent assessments of technologies.

Entrepreneurial research hubs

Research is needed to elucidate issues such as social and behavioral acceptance and understanding of commercialization needs. Entrepreneurial research hubs could support links between fundamental research and market needs.

Pilot plant facilities

Research is needed at pilot plant facilities to reduce the risks involved in the commercialization of new technologies. This could facilitate the development of technologies beyond the laboratory scale.

Increased exposure to issues experienced during scale-up could also highlight entirely new areas of research. Typically scale-up research is done in industrial research settings; however, industry may be unlikely to invest in development of these nascent technologies beyond the laboratory scale due to the lack of market, regulatory, and policy drivers. Therefore, government investment will be critical to enable these technologies to reach pilot and demonstration scale. Design and development of flexible pilot plant facilities to de-risk the commercialization of new technologies will be needed.

Advanced testing

Research is needed to develop predictive accelerated aging evaluation methodologies for mineral carbonation. Such models would help de-risk technologies and streamline their introduction into conservative market applications where extensive performance data are needed to establish codes for use.

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10

Criteria for Evaluating Carbon Utilization Technologies

Establishing criteria for evaluating the potential for commercialization of carbon utilization technologies facilitates both the identification of areas where research and development might be most impactful and comparison of different carbon utilization technologies. Decisions about whether to commercialize a product are complex. It is necessary to establish proof of value, that is, to determine if the technology either addresses a limitation of the current market (such as by lowering the cost or increasing the lifespan of a product) or fills a new need in the market. Issues associated with capital expenditure, regulations, and availability of feedstocks are all crucial and may vary depending on the location in which a new technology is being implemented. Commercialization considerations are also time dependent; a technology that is not commercially viable today may become so in the future because of market, policy, or societal changes. Similarly, regional factors may dictate commercial viability such that technologies that are commercially viable in one region may not be feasible elsewhere. Because carbon utilization involves goals related to the mitigation of greenhouse gas emissions, environmental considerations are also important for evaluating these technologies.

Factors relevant to assessing and commercializing carbon utilization technologies are discussed in Chapters 8 and 9. Key factors include the technology's potential economic value; its scale, market capacity, and market penetration; the ability to manage relevant external factors such as infrastructure and regulations; the potential unintended outcomes and consequences associated with the technology; the availability and suitability of the carbon waste stream to be used; the potential environmental and societal risks associated with using a carbon waste stream to generate products; and the associated life-cycle greenhouse gas impact. This chapter expands upon those 7 factors to develop 14 criteria for assessing the commercial viability of carbon utilization technologies.

Many of the criteria that are useful for assessing the commercial viability of carbon utilization technologies are similar to those that are useful for assessing any emerging technology. For example, whether a technology is economically competitive with an existing process to deliver an identical or functionally equivalent product is crucial regardless of whether the technology involves a carbon waste stream. Other criteria, such as the permanence of carbon capture in the end product, are unique to carbon utilization technologies.

In practice, different evaluators may weight these factors differently. For example, an evaluator whose main objective is to reduce atmospheric greenhouse gas concentrations would likely emphasize life-cycle greenhouse gas emissions over other factors. In contrast, if the primary objective is the rapid development of an economically feasible process to produce fuels or

products, criteria related to economic value, market factors, and external factors would receive greater emphasis.

Technology developers and research funding decision makers already use criteria similar to those outlined in this chapter to inform their decisions. For example, the NRG COSIA Carbon XPRIZE (see Box 10-1), Breakthrough Energy Ventures, and the Oil and Gas Climate Initiative have developed their own sets of criteria to incentivize and evaluate the advancement of carbon utilization technologies. Companies developing carbon waste–derived products apply similar criteria to guide product development and investment decisions (see Box 10-2). The factors and criteria outlined in this chapter guided the committee's assessment of technologies and research needs presented in the rest of this report and can be a useful framework for other evaluators in the future.

Box 10-1

Carbon XPRIZE Evaluation Criteria

The NRG COSIA Carbon XPRIZE is an international competition designed to accelerate the deployment of carbon utilization technologies. Teams develop technologies focused on utilizing carbon dioxide from either natural gas or coal-based flue gas streams. Their technologies are judged by the technical and business viability of their approaches at the fundamental research scale, pilot scale, and demonstration scale.

Judgment criteria include

(1) The amount of carbon dioxide that is converted into products,
(2) The net value of the products manufactured,
(3) The freshwater consumption, and
(4) The land use footprint.

These criteria illustrate one way that parties interested in advancing carbon utilization technologies evaluate and compare various candidate technologies. The XPRIZE criteria are in many ways related to the factors and criteria outlined in this report, though they are not identical. For example, XPRIZE criterion 1 parallels but is less holistic than life-cycle greenhouse gas impact, which includes carbon dioxide uptake and permanence of sequestration. In order for teams to address criteria 1 and 2, they are required to assess factors related to economic value, scale, market capacity, and market penetration. XPRIZE criteria 3 and 4 are relevant to evaluating unintended outcomes and consequences and factors identified by the committee.

Box 10-2

Covestro's Development of Carbon Waste–Derived Foams

Covestro is a global supplier of polymer materials that has been experimenting with utilizing carbon dioxide as a building block for a variety of plastic materials to offset the use of traditional fossil resources for the same products. In 2016 the company began marketing their polyol, cardyon®, that is built from up to 20 percent carbon dioxide sourced from an adjacent chemical plant, for use in the flexible foam market (http://press.covestro.com/news.nsf/id/covestro-starts-brand-launch-for-co2-products). Belgian manufacturer Recticel became the first industrial partner to use the cardyon® polyol, offering mattress products https://www.chemanager-online.com/en/news-opinions/headlines/recticel-first-user-covestro-co2-polyol in the European market since late 2016. The cardyon polyol is currently made in a 5,000 tons/yr facility. The product is at the beginning of the commercialization stage, with the plant operating on the order of 1/100th (or 1 percent) of the size of a typical polyol facility. The company has announced plans for a 100 kt/yr plant, which, though 20 times larger than current production, would still be a small plant by current industry standards.

Covestro used several factors to evaluate the carbon utilization technology and market potential before pursing polyols targeted for the flexible foam market. For example, developers assessed economic value, scale, market capacity, market penetration, and control of external factors such as waste stream source, quality, quantity, and siting. This assessment led the company to focus on flexible foams, the largest segment of the polyurethane market. An evaluation of the life-cycle greenhouse gas (GHG) reductions of flexible foam mattresses was completed to evaluate the level of GHG emissions from polyol production, which were 2.6-2.9 kg CO_2e/kg and so not net negative in carbon emissions. However, a comparison of these emissions to those from conventional polyol production revealed that these emissions were between 0.4 and 0.6 kg CO_2e/kg less than those of conventional polyols. So, while the polyols from waste CO_2 are not a carbon sink, producing them from waste gaseous carbon would result in a GHG reduction as compared to producing them conventionally.

As a result of this assessment, Covestro concluded that their carbon dioxide–derived polyol for use in flexible foam mattresses had improved environmental attributes and similar performance characteristics, to conventionally produced polyols, resulting in adequate market penetration.

FACTORS FOR EVALUATION OF EMERGING TECHNOLOGIES, INCLUDING CARBON UTILIZATION

Many factors commonly used to evaluate other types of emerging technologies are relevant to carbon utilization technologies as well. The following sections describe criteria that can be used to evaluate these factors in the context of carbon utilization.

Economic Value

To be commercially viable, any product produced from a carbon waste stream eventually needs to be economically feasible; that is, it must be possible to generate a return on investment. Some factors that impact whether a product will be economically feasible include the cost of the raw material required for the process, the cost of building and operating the equipment and infrastructure required for the process, and the value of the product. If a new technology represents a direct replacement for an existing process or product, it likely needs to be economically competitive with existing technology to be commercially viable. For example, if a product made

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using an existing technology can be sold at a lower price than an equivalent product made from carbon waste, it is unlikely that the product produced from carbon waste will be commercially viable unless there is a differentiation for the product that can be promoted to justify its higher price. Alternatively, if a technology is in a new market, there needs to be a demand for the product for it to be commercially viable. In some cases, it may be possible for policy and regulations to influence a product's commercial viability, for example a carbon tax. Tecommending policy changes is outside the scope of this report, however lessons may be learned from the experience of the European Union in cap and trade of carbon emissions. Since 2005, the European Union has operated an emissions cap and trade system, however carbon waste gas utilization does not qualify for credits. Beginning in 2021, a portion o the system revenues will fund an innovation fund which will include research and development investments in CCU[1]. The funded projects will be a source of learning for the research and policy communities in Europe and elsewhere, including the United States. Overall, in determining economic feasibility it is important to consider both the inherent economic value of a new technology and its ability to compete with current products.

Evaluation criteria include the following:

- Is the selling price of the carbon-derived product significantly lower than that of its direct competitors in the market?
- Would a company earn a sufficient internal rate of return from producing the carbon-derived product?

Scale, Market Capacity, and Market Penetration

Criteria relevant to scale, market capacity, and market penetration are useful for evaluating the potential volume and market share of a new product, as well as its ability to compete with existing products in the same market niche.

Scale and Market Capacity

The scale at which a new technology can be implemented is an important criterion for determining the commercial viability, degree of commercial success, and carbon emissions mitigation potential of a product. Some technologies require scientific challenges to be solved for production to occur at volumes needed to meet market demand, for example, limitations associated with mass transfer and reactor design. These technological barriers are discussed in Chapters 3-6, and only the market demand itself is considered in this chapter.

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[1] See https://ec.europa.eu/clima/policies/ets/revision_en.

In considering the scale of market demand for a product, it is important to not just consider the current volume of a product that is produced but the overall potential market capacity. For example, the market capacity for a new product could be significantly larger than the current scale at which the product is produced if it can provide an alternative to a different product that is made at significant scale. A specific example of this principle is oxalic acid (see Box 10-3). While oxalic acid is currently produced at a small scale in part because it is difficult to synthesize, it could potentially displace other chemicals as a feedstock if it could be made more efficiently. This means that the market capacity for oxalic acid is potentially much greater than the current scale at which it is synthesized.

Box 10-3

Oxalic Acid
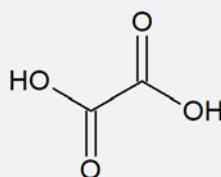
Oxalic acid is most widely used as a bleaching or cleaning agent in the textile and wood industries. It can also be used as a rust remover, used to make ethylene glycol (a heat transfer fluid and a precursor to common plastics), and used in the pharmaceutical industry. Currently oxalic acid is produced at a small scale due to various synthetic challenges, thus resulting in a limited market. The market capacity for oxalic acid has the capacity to change if it could be prepared more efficiently. By doing so, oxalic acid could displace other chemicals as a feedstock, and its market size could increase.

Evaluation criteria include the following:

- In what volumes is the product currently made through conventional means?
- What is the potential market capacity of the analogous carbon utilization–derived product?

Market Penetration

When a new technology is competing with an existing technology, the potential market penetration of the new product is a crucial criterion in assessing its commercially viability. The key issue is the new product's ability to capture market share that currently belongs to an incumbent product made using conventional technology. Cost and availability of raw materials and the ability to effectively transport feedstocks and end products have influenced not only the siting but also the economic viability of commodity process facilities for decades. Some processes may face technical challenges to scale-up that could increase costs for implementation at meaningful production volumes and could impact the technology's ability to gain market share.

Such technical challenges are discussed in Chapters 3-6, and the economic considerations for commercialization are discussed in this chapter. In some cases, the ability to capture market share may be influenced by economic or regulatory factors that pertain to a certain region. For example, regional differences in the price of hydrogen or electricity may allow a product made from carbon waste to have significant market penetration in one area but not in others. This is exemplified by the production of methanol from gaseous carbon waste streams in Iceland, where electricity and hydrogen are available at much lower prices than elsewhere due to the country's hydroelectric and geothermal resources (see Box 10-4). Additional advantages for carbon utilization in this location include the high purity of the flue gas stream and policy directives from the European Commission that counteract the competitive edge fossil fuels would otherwise have over methanol in transport fuel applications. While the Icelandic situation is unique in many aspects, the country's success demonstrates how certain economic, policy, or social environments could increase the likelihood that a new product will displace existing ones.

Evaluation criteria include the following:

- Would the carbon waste–derived product be expected to achieve substantial market penetration within years, or would it take decades?

Box 10-4

Methanol Production in Iceland

Currently, as described in Chapter 5, methanol is produced directly from CO_2 and H_2 in Iceland. However, this technology is only commercially viable in Iceland for three reasons:

(i) The cost of electricity in Iceland is significantly lower than in other locations as they have ready access to hydro and geothermal energy. This provides a renewable and inexpensive source of H_2.

(ii) The flue gas stream utilized is very highly concentrated in CO_2 relative to typical flue gas streams.

(iii) The European Commission has policy directives on the amount of transport fuel which must come from renewable resources. As a consequence, methanol derived from CO_2 does not have to compete directly with fossil fuels and is economically feasible when compared to biofuels and other renewable fuels sources.

This unique situation is not replicated in other parts of the world and as a consequence the production of methanol from CO_2 and H_2 is not currently feasible in other locations.

Control of External Factors

For many technologies, control of external factors associated with the technology (often referred to as the value chain) is crucial for commercial viability. For example, if a company wants to develop a carbon utilization technology but does not control the pipeline bringing the waste carbon feedstock to the production site, risks to the process may increase and the technology may

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be less economically feasible. It is beyond the scope of this report to identify all of the factors associated with control of the value chain for every carbon utilization technology. In general, it is likely that regulatory factors will influence the commercial viability of many of these technologies. For example, if carbon dioxide is mineralized to produce cement, the chemical composition of the cement changes, and building codes will need to be updated before the carbon dioxide–derived cement can be utilized (see Box 10-5). Similarly, the impurities present in commodity chemicals are often tightly regulated, so if carbon waste–based processes for making those chemicals introduce impurities into the chemical products, changes to regulation may be required in order for the chemicals to be sold. Finally, biological carbon utilization technologies may encounter regulatory issues related to the use of genetically modified organisms in open water streams. These examples highlight the fact that, even if a new technology is scientifically sound, other factors could undermine its commercial viability.

Evaluation criteria include the following:
- Does the producer of the technology have nearly full control of the value chain, or only a small portion of it?

Box 10-5

Impact of Codes and Standards in the Building Materials Market

Among other external factors, a new technology may be subject to codes and standards that are outside of the control of the firm marketing the technology. The building materials market highlights one example. Carbonates used in construction include concrete (used in buildings and roads) and aggregate (used in concrete, asphalt, and roadbeds). Such construction materials typically must meet composition-based and/or performance-based codes and standards for use. These codes and standards may inhibit or delay introduction of new materials, such as those made with carbon dioxide, that meet or exceed performance requirements but are made in a novel way that differs from the composition standard. Compounding the problem, many construction industry standards are unique to particular industries, applications, or locales, such as individual U.S. state building codes. For the product to grow into new markets, the relevant industry or locality-based standards will need to be changed, sometimes individually. Introducing new codes and standards is a significant barrier to the introduction of new construction materials subject to composition-based standards and represents an important factor for evaluating commercial viability.

Unintended Outcomes

It is also vital to consider potential unintended outcomes and consequences of deploying a new technology. Although these are inherently often difficult to foresee, it is sometimes possible to avoid negative impacts by anticipating counterintuitive outcomes or understanding how a new technology might affect apparently unrelated areas. An example of this principle from environmental economics is known as the Jevons paradox, which stipulates that increases in efficiency often lead to increases in consumption, so the expected benefits of the more efficient process are not realized. In the chemical industry, changes in the type of feedstock can have

unintended consequences. For example, by changing the cost of chemical industry feedstocks the shale gas boom has affected the economic viability of multiple technologies, as illustrated in Box 10-6 (DeRosa and Allen, 2016). Similar consequences could occur if waste carbon dioxide were to become widely used as a feedstock for fuels and products. Furthermore, if technologies that use carbon dioxide have a significant impact on land use or water consumption, their widespread adoption could result in increased carbon dioxide emissions from land carbon stocks or could cause water scarcity issues.

Evaluation criteria include the following:

- Could the technology cause large market disruptions that could alter land and water use patterns, chemical industry structure, or fuel usage patterns?

Box 10-6

Unintended Consequences of Shale Gas Development

During the mid 2000s, chemical manufacturing plants were being built worldwide with more than $1 billion in capitalization; however, none were under construction in the United States. In fact, the U.S. chemical industry was in a decline, and chemical plants were being disassembled and moved to production sites abroad.

This apparent decline, however, was counterbalanced by an unexpected factor that emerged around the same time. Oil and gas from shale deposits in the United States were found to be recoverable at economically viable rates. The increase in shale gas production resulted in abundant and affordable domestic supplies of natural gas and associated liquids. Use of shale gas products transformed the U.S. chemical industry from one of the world's highest-cost producers in 2005 to one of the lowest-cost producers today. The shift from heavier petroleum-based feedstocks to lighter shale gas sources changed the relative availability and cost of certain chemicals. For example, while the cost of ethylene has dropped, the prices of butadiene and aromatic chemicals such as benzene and toluene—all byproducts of naphtha/oil cracking to produce ethylene—increased as supplies became constrained with the shift from naphtha to natural gas liquid feedstocks.

With the abundance of low cost natural gas and associated liquids in the United States, direct conversion of natural gas and natural gas liquids into value-added chemicals with a lower carbon footprint will be enabled by the discovery and development of new catalysts and processes. Similar disruptive consequences could occur if waste CO2 were to become widely used as a feedstock for fuels and products.

CRITERIA SPECIFIC TO CARBON WASTE UTILIZATION

In addition to factors that are commonly considered when assessing any emerging technology, the viability of carbon utilization technologies also depends on factors that are unique to the use of carbon waste as a feedstock or unique to technologies that are intended to reduce greenhouse gas emissions.

Availability and Suitability of Waste Stream

The economic viability of carbon utilization technologies depends on the volume and quality of carbon waste available (see Box 10-7). This determines the suitability of available inputs as well as the scale of production that can be achieved. Tolerance to change in the quality of inputs can also influence viability; for example, a CO_2 process that is immune to changes in the waste stream composition (e.g., if the type of coal used in a power plant is changed) is more robust and has a higher likelihood of viability. The availability and quality of carbon dioxide waste streams is discussed in Chapter 2.

Evaluation criteria include the following:

- Is a sufficient quantity of carbon waste available at the required quality to produce the product at a cost that enables competitive market pricing?
- Would changes in the carbon waste stream cause substantial changes in yield or purity of the product?

Box 10-7

Availability and Suitability of Waste Streams

Some carbon utilization technologies can valorize species other than carbon dioxide and methane in waste gases, making the impurity of the waste gas stream a benefit. For example, Lanzatech uses microbes that convert carbon-rich waste gases containing carbon monoxide, hydrogen, carbon dioxide, methane, and other species into a variety of products. The microbes use carbon monoxide as an energy source; this carbon monoxide would otherwise need to be treated as an air pollutant, and this avoided cost increases the economic benefit of the carbon utilization technology.

Risks Associated with Use of Waste as a Feedstock

Depending on their source, gaseous carbon waste streams can contain contaminants including toxic materials. While separation processes can be designed to remove these materials, there is a risk for process failure that could lead to incorporation of contaminants into the final product. This risk can lead to commercialization barriers ranging from negative consumer perceptions to regulatory restrictions. Such risks may be less impactful for some products, such as fuels (assuming the product still meets fuel quality specifications and the toxic materials are destroyed in the combustion process), but more impactful for products like pharmaceuticals or consumer products, which can be subject to strict safety standards and more vulnerable to consumer perception.

Evaluation criteria include the following:

- Is the product subject to regulatory constraints relevant to the use of a waste feedstock in its production?
- Would contamination in the product pose a threat to human health?

Life-Cycle Greenhouse Gas Impact

Carbon utilization technologies are often viewed through the lens of mitigating carbon emissions. While carbon utilization is indeed an important strategy to make use of a widely available waste stream toward a circular carbon economy, not every utilization technology will offer significant levels of reduction in greenhouse gas emissions or act as a net carbon sink (see Box 8-1, Chapter 8). Nonetheless, fuels and products from carbon utilization may be lower emitting on a life-cycle basis compared to conventional fuels and products through, for example, increased processing efficiency, replacement of energy-intensive feedstocks or reactants with carbon waste–enabled process chemistry, or the exploitation of renewable electricity or hydrogen. Some carbon utilization processes may consume less energy or water or produce fewer air pollutants than conventional processes for making the same products. In addition, the extent to which waste carbon is incorporated into a product and the permanence of that uptake can play an important role in the utilization technology's overall greenhouse gas impact.

Life-cycle assessment (LCA), as described in Chapter 8, is useful for assessing energy and environmental impacts as part of the process of evaluating carbon utilization technologies. Different approaches may be appropriate at various stages of technology development; for example, attributional LCA (essentially a step-by-step accounting of the energy and environmental burdens associated with each step of the supply chain) is an appropriate framework in earlier stages, whereas a consequential LCA (which takes into account how a disruptive technology may shift material and energy flows in a part of or all of the economy) may be useful later in the development process to anticipate and address potential unintended outcomes. In either case, it is important to use common and transparent assumptions in the analysis and common emissions factors to describe the emissions associated with various inputs and processes in order to accurately compare carbon utilization technologies with conventional processes.

Evaluation criteria include the following:

- Are the life-cycle greenhouse gas emissions, water consumption, and air pollutant emissions of the carbon utilization–derived product advantageous compared to the same or functionally equivalent product produced conventionally? If some of these aspects are not favorable, what is the potential or cost to mitigate those aspects (e.g., through pollution control, water reuse, or other technology)?

- What is the total potential for carbon uptake into the product, given the product's market potential and the amount of waste carbon incorporated per unit mass produced?
- Will carbon be stored in the product for the short term (less than 1 year), medium term (up to a decade), or long term (decades)?

CONCLUSIONS

This chapter outlines 7 factors and 14 criteria (summarized in Table 10-1) that are useful to consider when assessing carbon utilization technologies to inform decision making for research funding, product development, or other purposes. While it will not be possible to evaluate every criterion when a technology is at the bench scale, evaluating emerging technologies where possible early in their development will give the first indications of potential commercial viability. As the technology progresses to the pilot and demonstration scales, additional criteria can be addressed to evaluate its potential to move into the commercial arena. In some cases, it is sufficient to evaluate the criteria at only one stage of development. For example, if the market for a given product is small when technology is at the bench scale, it is likely to remain so and this criterion would not need to be revisited. For other criteria, multiple evaluations may be needed as the technology matures. For example, the results of life-cycle assessments may evolve as more insights are gained into factors such as yield, selectivity, and energy consumption.

TABLE 10-1 Factors to consider when assessing carbon utilization technologies and criteria for evaluating those factors.

Factors	Criteria
Economic value	• Is the production cost of the carbon utilization–derived product competitive with the production cost of its immediate competitors in the market?
	• Would a company earn a sufficient internal rate of return from producing the carbon waste–derived product?
Scale, market capacity, and market penetration	• In what volumes is the product currently made through conventional means?
	• What is the potential market capacity of the analogous carbon-derived product?
	• Would the carbon waste–derived product be expected to achieve substantial market penetration within years, or would it take decades?
Control of external factors associated with the technology	• Does the producer of the technology have nearly full control of the value chain, or only a small portion of it?

Unintended outcomes and consequences	• Could the technology cause large market disruptions that affect areas such as land and water use patterns, chemical industry structures, or fuel usage patterns?
Availability and suitability of waste stream	• Is a sufficient quantity of carbon waste available at the required quality to produce the product at a cost that enables competitive market pricing? • Would changes in the carbon waste stream cause substantial changes in yield or purity of the product?
Risks associated with the use of waste as a feedstock	• Is the product subject to regulatory constraints relevant to the use of a waste feedstock in its production? • Would contamination in the product pose a threat to human health?
Life-cycle greenhouse gas reductions	• Are the life-cycle greenhouse gas emissions, water consumption, and air pollutant emissions of the carbon utilization–derived product advantageous compared to the same or functionally equivalent product produced conventionally? • What is the total potential for carbon uptake into the product, given the product's market potential and the amount of waste carbon incorporated per unit mass produced? • Will carbon be stored in the product for the short term (less than 1 year), medium term (up to a decade), or long term (decades)?

REFERENCE

DeRosa, S. E., and D. T. Allen. 2016. Impact of new manufacturing technologies on the petrochemical industry in the United States: A methane-to-aromatics case study. *Industrial & Engineering Chemistry Research* 55:5366-5372. doi: 10.1021/acs.iecr.6b00608.

11

Research Agenda

INTRODUCTION

Some analyses have indicated that products derived from carbon utilization could create a market as high as $800 billion, utilizing 7 billion metric tons of gaseous carbon waste per year by 2030 (CO$_2$ Sciences, Inc., 2016). Utilization of gaseous carbon waste streams to make valuable products has the potential to offset the cost of carbon capture and move society toward a more circular carbon economy. However, realizing this potential will require a variety of technological advances. Streams of gaseous carbon waste, currently produced at the scale of tens of billions of metric tons per year, are widely distributed and heterogeneous. Many carbon utilization technologies will require separation and purification of these waste streams, and some utilization processes may require additional enabling technologies, such as low-carbon methods for generating electricity or hydrogen. Additional barriers relate to characterizing waste gas streams, implementing carbon utilization technologies at commercial scales, efficiently transporting inputs or products, and creating economic value while achieving a net reduction in greenhouse gas emissions.

This chapter outlines a research agenda to address all aspects of the carbon utilization system (see Figures 11-1 and 11-2). While some research needs are specific to particular inputs (such as carbon dioxide or methane) or to particular processes (such as mineralization, chemical conversion, or biological conversion), other research needs are cross-cutting. A broad review of all aspects of the carbon utilization system was taken in order to develop a high-level research agenda. Specific technology barriers have been highlighted throughout Chapters 3-7. In addition, research is needed to improve the applicability of analysis tools such as life-cycle assessment and technoeconomic analysis for transparently evaluating carbon utilization technologies. The proposed research agenda is based on waste streams and enabling technologies and resources available in the United States but is broadly applicable to ongoing research efforts supported by multiple national and international entities.
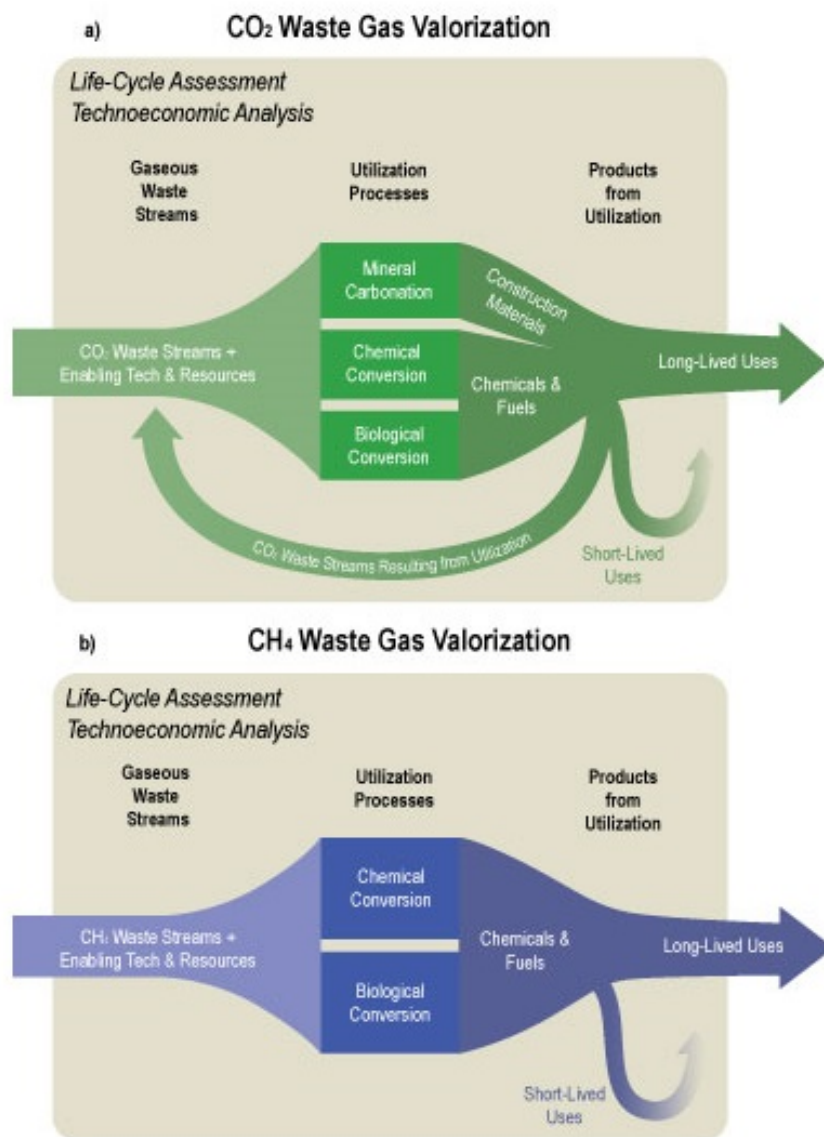
FIGURE 11-1 Overview of the carbon utilization system for both (a) carbon dioxide waste streams and (b) methane waste streams, including inputs of waste gases, enabling technologies and resources, and utilization processes and products. Utilization processes and products have the potential to generate significant economic value and reduce greenhouse gas emissions. Tools such as life-cycle assessment and technoeconomic analysis provide frameworks for evaluating economic, environmental, and other impacts of carbon utilization.

> **Recommendation 1: In order to realize potential benefits including improved energy and resource efficiency, creation of valuable industrial products, and mitigation of greenhouse gas emissions, the U.S. government and the private sector should jointly implement a multifaceted, multiscale research agenda to create and improve technologies for waste gas utilization.**

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Specifically, the U.S. government and the private sector should support

- Research and development in carbon utilization technologies to develop pathways for making valuable products and to remove technical barriers to waste stream utilization;
- The development of new life-cycle assessment and technoeconomic tools and benchmark assessments that will enable consistent and transparent evaluation of carbon utilization technologies; and
- The development of enabling technologies and resources such as low- or zero-carbon hydrogen and electricity generation technologies to advance the development of carbon utilization technologies with a net life-cycle reduction in greenhouse gas emissions.

RESEARCH AGENDA

The committee identified priority research in three main areas: needs related to the gaseous carbon waste streams that represent the main inputs for carbon utilization technologies, needs related to utilization processes that convert these inputs into valuable products, and needs related to evaluating utilization technologies in order to support transparency and informed decision making.

Research Needs Related to Carbon Inputs

Gaseous carbon waste streams are heterogeneous in their composition. This poses a challenge for carbon utilization processes that require pure inputs. Waste gas separation and purification technologies enable many types of carbon utilization by concentrating valuable reactants and products and by removing contaminants that may damage catalysts or otherwise impede productivity. While cryogenic distillation and other technologically mature separation processes may be effective for this purpose, research and development is needed to advance alternative techniques with reduced energy requirements, cost, and greenhouse gas footprints. In addition, there is a need for methods to regenerate solvents and sorbents used in capturing carbon from gaseous waste gas streams.

While some carbon utilization processes require pure feed streams, other utilization processes valorize species in addition to carbon dioxide and methane, in which case impure gaseous waste streams can be beneficial and separation or purification may not be necessary, reducing capital costs and energy requirements. However, because detailed characterizations of waste stream compositions are not widely available and the tolerance of carbon utilization processes for impure carbon dioxide and methane feeds is not generally known, it can be challenging to determine separation and purification requirements. In addition, most current carbon utilization activities take an opportunistic approach to accessing waste streams, rather than a systematic approach to match waste streams with the utilization processes for which they are

best suited. Separation and purification targets must be integrated with information about the waste stream and processes to be used, including carbon capture techniques, requiring an integrated approach.

Priority research areas include the following:

> *Gaseous carbon waste mapping.* Research is needed to map the detailed compositions and magnitudes of gaseous carbon waste streams, with particular attention to co-emitted species that could either hinder or enhance carbon utilization processes. This could increase opportunities for matching waste streams with appropriate utilization processes.

Research Needs Related to Utilization Processes

Carbon utilization processes are in various stages of development and commercialization. The committee identified research needs relevant to advancing carbon dioxide, methane, and biogas utilization in the context of three main utilization pathways: mineralization, chemical conversion, and biological conversion. In addition to these specific research needs, the committee identified two main areas in which additional research and development would yield benefits across all utilization technologies: process system improvement and improved catalysis.

Development of commercial processes requires not just fundamental research advances but also process system improvement. Process system improvements may include, for example, more efficient techniques for mass transport or solvation of gaseous waste, better process monitoring techniques, and process intensification and optimization. They may also include techniques for better integrating carbon utilization processes with carbon capture technologies, integrating catalysis research with reactor design, or managing and recycling inputs or products to minimize waste.

Improving catalysis and catalytic technologies is another research area that could benefit multiple utilization pathways. For example, in mineralization, there is a need to develop catalysts for accelerating carbonation based on control and distributions of surface sites for reactions. In chemical utilization, there is a need for improved catalysts that use sustainable raw materials (e.g., abundant elements such as iron or nickel) rather than scarce and costly noble metals, for which production tends to have a higher carbon footprint. In biological utilization, catalysts are needed for hydrogenation of lipid extracts, which can be a limiting factor for commercial-scale adoption. In electrocatalysis, catalytic technologies are needed to reduce the cost and complexity of product recovery, as well as to reduce toxicity to the host organism in bioelectrochemical processes.

The following sections outline additional key research needs specific to various utilization technologies and inputs.

Mineralization of Carbon Dioxide

Mineralization processes use waste carbon dioxide to produce construction materials including aggregates and cement. Compared to other carbon utilization processes considered in this report, mineralization offers the greatest potential for utilizing large quantities of carbon dioxide in the short to medium term because (1) mineral carbonation reactions are thermodynamically favored and therefore require little if any extrinsic energy, and (2) because building materials are used at scales of billions of tons per year and have long product lifetimes, mineralization represents a significant opportunity for long-term carbon sequestration in addition to being an opportunity for carbon utilization. The technology for mineralization processes is already being practiced at limited commercial scale, but further research and development is needed. For example, while the formation of calcium and magnesium carbonates can be accomplished by contacting carbon dioxide with many alkaline reactants in the presence of water, it is important to identify reactants that are available in large quantities, will carbonate sufficiently and quickly, and can be produced at low energy and economic cost. In addition, it is necessary to determine the engineering properties and chemical durability of carbonated building materials before these products can find use in construction markets.

Priority research areas include the following:

> *Controlling carbonation reactions*. Research is needed to understand the fundamental chemical features that control the relative rates of carbonation and hydration. This could lead to improved selection of alkaline solids and reaction conditions.

> *Process design*. Research is needed to integrate mineralization processes with existing carbon dioxide capture technologies. This could lead to improved process performance and ensure optimal carbon dioxide conversion rates and energy use efficiencies.

> *Accelerating carbonation and crystal growth*. Research is needed to develop additives for enhanced carbon dioxide solubility or structure-directing agents that accelerate particle growth. This could accelerate carbonation reactions such as crystal growth rates in solution beyond what is achieved simply by increasing the pH.

> *Green synthesis routes for alkaline reactants*. Research is needed to develop energy- and carbon dioxide–efficient pathways and processes for producing alkaline solids that can be readily carbonated and do not require high-temperature activation. This could lead to energy- and carbon dioxide–efficient pathways.

Structure-property relationships. Research is needed to develop physical and instrumental assessment methods, improved modeling, and performance-based criteria for product properties. This could improve predictions of structure-property relations and increase the durability, viability, and acceptance of carbonated solids.

Analytical and characterization tools. Research is needed to develop new analytical tools for studying carbonation reactions in dense and viscous suspensions, as well as the evolution of microstructure across length scales. This could lead to new scientific tools to characterize mineralization technologies.

Construction methodologies. Research is needed to develop new material formulations with novel properties and to advance the use of additive manufacturing to construct components with superior strength-to-weight ratio, optimized topology, and more complex geometries compared to what can be made with existing construction methods. This could enable new categories of carbon utilization products.

Chemical Conversion of Carbon Dioxide

Chemical conversion of carbon dioxide to make chemicals and fuels offers opportunities to improve upon existing processes and potentially develop new markets. However, there remain significant challenges to chemical carbon dioxide utilization pathways, including the low energy of carbon dioxide, the need to build carbon-carbon bonds, impurities in gaseous waste streams, and the lack of durable and highly reactive catalysts for processes of interest.

Priority research areas include the following:

Chemical catalysis. Research is needed to improve existing catalysts or discover entirely new catalysts. In addition to the usual performance metrics (activity, selectivity, durability), special attention should be given to designing catalysts that tolerate the impurities present in carbon dioxide–containing waste streams to avoid costly and energy-intensive carbon dioxide purifications.

Avoiding stoichiometric additives. Research is needed to avoid stoichiometric additives that are not integrated into products, or to identify additives that are easily regenerated. This could lead to processes that generate limited waste for commodity chemical or fuel production.

Integrating catalysis and reactor design. Research is needed to integrate catalysts with the most efficient reactor including the identification of factors that affect

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catalyst performance at synthetically relevant rates. This could accelerate the development of carbon dioxide conversion processes that are relevant at the commercial scale.

Pathways to new products. Research is needed to develop processes that produce nontraditional targets, especially those with carbon-carbon bonds. This could transform processes for producing a wide range of chemicals and could create new markets.

Coupling oxidation and reduction reactions. Research is needed to combine carbon dioxide reduction with the oxidation of substrates from other waste streams (e.g., agricultural or biomass waste). This could open new pathways to reduce the cost of carbon dioxide conversion and create multiple high-value products.

System engineering and reactor design. Research is needed to develop reactor technologies that are tailored to the demands of carbon dioxide conversion processes. For example, reactors that allow for very efficient removal of products that are formed at low conversion for thermodynamic reasons would be beneficial. For electrochemical conversions, reactors that optimize single-pass conversion would mitigate the costs of product separation. Systems that integrate carbon dioxide capture with conversion also need to be explored to minimize the steps required for waste gas valorization.

Biological Conversion of Carbon Dioxide

Biological processes including photosynthesis and nonphotosynthetic processes offer numerous opportunities for converting carbon dioxide into chemicals and fuels. Cyanobacteria are a particularly promising platform for biological conversion because of their photosynthetic efficiency and genetic manipulability, but additional research is needed in order to improve titers and make cyanobacteria-based processes scalable and economically viable. Nonphotosynthetic biological carbon utilization systems avoid the use of high-cost carbohydrates and can be manipulated to create a wide variety of products. Electrocatalysis, either through direct or indirect transfer of electrons, also holds promise because the electricity can help overcome the inherent inefficiency of photosynthesis.

Priority research areas include the following:

Bioreactor and cultivation optimization. Research is needed to improve bioreactor system design for efficient carbon dioxide solvation, mass transfer, dewatering and harvesting, and management and recycling of water and nutrients. This may include

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development of better computational and modeling tools for optimizing cultivation processes. Advancement of nonphotosynthetic methods may require novel bioreactor design in order to incorporate new feedstocks or hybrid fermentative systems. This could improve culture-monitoring technologies and facilitate scale-up of utilization.

Analytical and monitoring tools. Research is needed to improve culture-monitoring technologies. This could facilitate scale-up.

Genome-scale modeling and improvement of metabolic efficiency. Research is needed to develop and improve methods for in-depth computational modeling, genetic manipulation, biochemical validation, and fermentative demonstration. This could improve metabolic flux, including carbon dioxide uptake and incorporation, photosynthetic efficiency, metabolic streamlining, and product accumulation.

Bioprospecting. Research is needed to accelerate the identification and characterization of organisms or biological systems with unique attributes such as carbon dioxide uptake, various product profiles, photosynthetic efficiency, and environmental tolerance. This could enhance the ability to produce target products in diverse geographic locations.

Valorization of co-products. Research is needed to develop feed and food uses for co-products of biological conversion, including studies in product safety and acceptability. This could improve the efficiency of energy and materials use and increase the economic value of biological conversion technologies.

Genetic tools. Research is needed to enhance engineering of photosynthetic and nonphotosynthetic organisms, including expansion of tools for genetic incorporation, selectable markers, promoter elements, protein folding and stability, and posttranslational control. This could improve efficiency and rates of biomass production and selective product formation.

Pathways to new products. Research is needed to identify biological pathways to produce nontraditional products and new products for unmet needs in commodity and specialty chemicals. This could expand the portfolio of products made via carbon utilization.

Methane and Biogas Utilization

Methane is a major component of several types of gaseous carbon waste streams, including waste gas from oil and gas supply chains (in which methane is typically mixed with other low-molecular-weight hydrocarbons) and biogas from landfills, manure, sewage, and other waste management operations (which are produced by microbes and consist primarily of carbon dioxide and methane). Existing methane and biogas utilization technologies have generally focused on direct utilization of methane as fuel; however, there are also opportunities to convert methane or biogas to other products through chemical or biological conversion. In general, the research needs of these processes parallel the research needs for utilization of carbon dioxide. For chemical pathways, priority research areas include better catalysts, methods for avoiding stoichiometric additives, approaches to integrate catalysis research with reactor design, and other process optimization methods (chemical research needs 1, 4, and 6). For biological processes, priority research areas include methods to improve solvation, mass transfer and delivery, metabolic flux, genetic engineering techniques, and valorization of co-products, as well as the identification of organisms or biological systems that may be useful for conversion processes (biological research needs 1-7).

Research Needs for Evaluating Utilization Technologies

Robust analytical tools are important for comparing technologies, evaluating viability, and informing decision making. While established tools such as life-cycle assessment and technoeconomic analysis are useful for this purpose, additional research is needed to facilitate the accurate, consistent, and transparent application of these tools to carbon utilization technologies.

Life-Cycle Assessment

Effective evaluation of the environmental burdens of utilization processes across the full life cycle of the process and its products will consider all materials, heat, electricity, and energy-carrying material inputs, as well as the final use and disposal of the product. Evaluation of carbon utilization technologies can reflect local conditions as well as the operation of infrastructures that support utilization processes, including both infrastructures that exist currently and those that will need to be developed in the future.

Priority research areas include the following:

> *Life-cycle assessment benchmarking*. Research is needed to develop benchmark life-cycle assessments of waste gas generation, waste gas cleanup, waste gas transport, electricity inputs, hydrogen inputs, and other enabling technologies to

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facilitate consistent and transparent assessments of the net greenhouse gas emissions of carbon utilization technologies. These benchmark assessments would include multiple environmental attributes of carbon utilization life cycles, such as greenhouse gas emissions, water use, air emissions, and materials use. This could lead to more consistent assessments of technologies.

Life-cycle analysis of emerging waste carbon utilization technologies. Research is needed to learn from transparent life-cycle analyses of emerging technologies, taking into account a system boundary that includes waste gas capture and cleanup, the conversion process, use phase, and end-of-life considerations. Although life-cycle assessment (LCA) results for emerging technologies will undoubtedly evolve, LCA at this early stage will help guide research toward activities that will heighten energy and environmental benefits.

Assessment of disruptive change. Research is needed to develop life-cycle analysis tools that move beyond assessing marginal changes in existing, static systems and address disruptive changes resulting from large-scale carbon utilization. This will provide tools for assessing disruptive changes necessary for performing consequential LCAs of carbon capture and utilization (CCU) systems.

Technoeconomic analysis

Technoeconomic analysis is an important tool for assessing the commercial viability of technologies. Documenting benchmarks would make technoeconomic analysis a more consistent and transparent tool for carbon utilization. Benchmarks needed include the cost, quantity, and purity of the available carbon dioxide stream, the cost and availability of other inputs such as hydrogen and electricity, and the quality of the product made and its marketability at the desired price. Other relevant considerations include market assessment, perception evaluation, and legal, regulatory, and policy issues, all of which can affect the deployment and acceptance of new technologies.

Priority research areas include the following:

Technoeconomic assessment benchmarking. Research is needed to develop standardized, transparent inputs and assumptions for technoeconomic analysis implemented for carbon utilization. This could lead to more consistent assessments of technologies.

Entrepreneurial research hubs. Research is needed to elucidate issues such as social and behavioral acceptance and understanding of commercialization needs.

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Entrepreneurial research hubs could support links between fundamental research and market needs.

Pilot plant facilities. Research is needed at pilot plant facilities to reduce risks involved in the commercialization of new technologies. This could facilitate the development of technologies beyond the laboratory scale.

Advanced testing. Research is needed to develop predictive accelerated aging evaluation methodologies for mineral carbonation. Such models would help de-risk technologies and streamline their introduction into conservative market applications where extensive performance data are needed to establish codes for use.

INTEGRATION WITH CURRENT RESEARCH ACTIVITIES

Research and development that is directly or indirectly relevant to carbon utilization is supported, directed, and performed in industry, academia, government, and the nonprofit sector. In the United States, research that impacts carbon utilization and enabling technologies is scattered throughout various federal research portfolios, including fundamental and applied research and development grant mechanisms administered by the Department of Energy (DOE), the Department of Defense, and the National Science Foundation, as well as through private-sector research and development programs.

Programs specific to carbon utilization include those at the DOE Office of Fossil Energy Clean Coal and Carbon Management program and projects within the Advanced Research Projects Agency–Energy (ARPA-E). The DOE Office of Fossil Energy funded a Carbon Use and Reuse project at $10 and $12 million in fiscal years 2017 and 2018, respectively,[1] within an overall budget of $95 and $98 million for the Fossil Energy Research and Development Carbon Storage and Utilization subprogram in fiscal years 2017 and 2018, respectively. ARPA-E programs fund high-risk, high-impact research and development projects in energy, including in chemical and biological carbon utilization and its enabling technologies. ARPA-E programs including Electrofuels, REMOTE, MARINER, PETRO, and REFUEL focus on forming fuels from methane or carbon dioxide. The agency's IMPACCT program focuses on carbon capture technologies. Together, those six programs supported 87 projects totaling $237.9 million in authorized funding.[2]

In addition to federal programs specifically designed to advance carbon utilization, various other research programs, including those overseen by DOE's Offices of Basic Energy Science and

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[1] See https://www.aip.org/fyi/2018/final-fy18-appropriations-doe-applied-energy-rd.
[2] See https://arpa-e.energy.gov/sites/default/files/ARPA-E_Annual_Reportfor_FY_2016_FINAL.pdf; https://arpa-e.energy.gov/?q=news-item/department-energy-announces-18-new-projects-accelerate-development-macroalgae-production; https://arpa-e.energy.gov/sites/default/files/documents/files/MARINER-Project-Descriptions-92117.pdf; https://www.nap.edu/read/24778/chapter/4; https://arpa-e.energy.gov/?q=program-listing.

Bioenergy Technologies, support fundamental research with strong connections to carbon utilization, for example, in the areas of catalysis, surface science, materials science, separations science, solar photochemistry, photosynthetic systems, and metabolism.

Private-sector funding for internal research and development programs relevant to carbon utilization includes efforts such as the NRG COSIA Carbon XPRIZE, which seeks to support and incentivize development and demonstration of breakthrough technologies in carbon utilization. Launched in 2015, the competition is expected to award a total of $5 million in milestone prizes and $15 million in grand prizes in 2020, as well as provide in-kind support for selected technology demonstration projects.

Outside of the United States, a number of other countries and organizations are funding carbon utilization research and development through dedicated funding and through regular research funding mechanisms. For example, life-cycle assessment research for carbon utilization is being conducted at RWTH Aachen University in Germany, and biological carbon utilization research is being conducted at the Flemish Institute for Technical Research as part of the European Horizon 2020 BIORECO2VER Project, among many other Horizon 2020 research programs on carbon waste gas utilization. Additional relevant research programs are under way in other parts of the European Union and in Japan. International partnerships are also growing, including a carbon capture utilization and sequestration (CCUS) initiative launched at the 2018 Clean Energy Ministerial forum to increase public-private partnerships in CCUS technology development. The new initiative is led by the DOE, Norway, and Saudi Arabia, and includes partners such as Canada, China, Japan, Mexico, Netherlands, United Arab Emirates, the United Kingdom, and the European Commission.[3] Related projects include the Carbon Sequestration Leadership Forum, the International Energy Agency (IEA), the IEA's Greenhouse Gas R&D Programme, Mission Innovation, and the Global CCS Institute.

The U.S. Congress has recently shown interest in stimulating use of carbon waste streams. For example, the FUTURE Act funds tax credits of between $10 and $35 per metric ton of carbon oxide utilized, for equipment put into service between 2016 and 2027.[4] In early 2018, a bill called the USE IT Act[5] was introduced that would support research on carbon utilization at the U.S. Environmental Protection Agency, streamline the permitting process for carbon utilization project developers, and expand on the tax credits available through the FUTURE Act.

There are important areas in which growth in research efforts could spur the technology development needed to achieve carbon utilization goals. The many existing research efforts and initiatives create fertile ground for the development of carbon utilization technologies, but the scattered nature of current efforts has the potential to leave gaps in the research portfolio. For example, different program goals will prioritize different factors and criteria in evaluating carbon utilization technologies. Coordination and communication are needed at multiple levels, across

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[3] See https://www.energy.gov/articles/department-energy-launches-two-new-clean-energy-initiatives-ninth-clean-energy-ministerial.
[4] See http://uscode.house.gov/view.xhtml?req=(title:26%20section:45Q%20edition:prelim)
https://www.congress.gov/bill/115th-congress/senate-bill/1535/all-info?r=1.
[5] See https://www.congress.gov/bill/115th-congress/senate-bill/2602.

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agencies, and between federal, private-sector, and nonprofit entities both nationally and internationally in order to accelerate research, development, and deployment of carbon utilization technologies. Examples of effective fora for communication and coordination include the Carbon Sequestration Leadership Forum[6] and Mission Innovation.[7]

> **Finding: Numerous research efforts relevant to advancing carbon utilization are under way both in the United States and abroad, supported by both public and private funding. Coordination and communication among existing carbon utilization research programs can lead to more rapid technology advancements.**

> **Recommendation 2: The U.S. federal science agencies should coordinate carbon utilization research and development efforts with private-sector activities in the United States and with international activities in the private and public sectors. Support for carbon utilization research and development should include technologies throughout different stages of maturity, from fundamental research through to commercialization, and evaluate them using a consistent framework of economic and environmental criteria.**

POTENTIAL FOR DISRUPTIVE CHANGE

The rationale for this research agenda is based on the assumption that large volumes of gaseous carbon waste, especially carbon dioxide, will continue to be generated in the coming decades through continued use of fossil fuels. However, carbon utilization may play a significant role in carbon management even if fossil fuels are largely replaced by low-emissions energy sources. In such a scenario, carbon utilization processes could involve the direct capture of carbon from the air. This has the potential to not just reduce emissions of greenhouse gases but actually remove greenhouse gases from the atmosphere. These types of scenarios could change the research agenda identified in this report.

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CO_2 Sciences, Inc. 2016. *Global Roadmap for Implementing CO_2 Utilization*. Available at https://assets.ctfassets.net/xg0gv1arhdr3/27vQZEvrxaQiQEAsGyoSQu/44ee0b72ceb9231ec53ed180cb759614/CO2U_ICEF_Roadmap_FINAL_2016_12_07.pdf (accessed October 10, 2018).

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[6] See https://www.cslforum.org/cslf/.
[7] See http://mission-innovation.net/.

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Appendix A

Glossary

Term	Explanation
Atom economy	The percentage of atoms in the starting reagents which are converted to product. A measure of the amount of waste products that are generated. Formally defined as atom economy = (molecular mass of product)/(molecular mass of all starting reagents) * 100.
Bench scale	A stage of commercialization where critical functions are proved and components or systems are validated in a laboratory environment and at a laboratory scale.
Biological utilization	Conversion of gaseous carbon wastes through biological processes.
Carbon capture	Carbon dioxide is captured at its point of production and separated from other by-products of fossil fuel combustion, compressed, and transported in a pipeline either for utilization or sequestration.
Carbon dioxide removal	The objective is large-scale removal of carbon dioxide from the atmosphere. Carbon dioxide removal approaches considered by the committee are coastal and land ecosystem management, accelerated weathering, bioenergy with carbon capture, direct air capture, and geologic sequestration.
Carbon utilization	The manufacture of valuable products from a gaseous carbon waste feedstock (carbon dioxide and methane) that results in a net reduction of greenhouse gases emitted to the atmosphere.
Chemical utilization	Conversion of gaseous carbon wastes through chemical processes.

Term	Explanation
Circular carbon economy	An industrial carbon-based system that is restorative or regenerative by intention and design.
Commercial–broad	A stage of commercialization where a product is manufactured in such a way that it does not rely on local environmental, regulatory, or other factors.
Commercial–limited	A stage of commercialization where a product is manufactured in an area with specific advantages that make it viable due to the local environmental, regulatory, or other factors.
Conversion	The amount of the starting material which is consumed in a reaction. Typically expressed as a percentage and defined as conversion = {1 − (amount of starting material at end of reaction)/(initial amount of starting material)} * 100.
Demonstration scale	A stage of commercialization where a full-scale system is demonstrated in a relevant environment.
Disruptive change	A change that creates a new market and value network that disrupts an existing market and value network.
Economic value	A measure of the benefit provided by a good or service to an economic agent.
Enabling resources	Resources such as hydrogen, electricity, and heat needed for carbon utilization.
Enabling technologies	Technologies such as transportation infrastructure and separations methods required for carbon utilization.
Energetic efficiency	The ratio, expressed as a percentage, of theoretical energy required (standard reduction / oxidation potential) multiplied by Faradaic efficiency to the actual energy required (standard reduction / oxidation potential plus overpotential). For an electrochemical process, the energetic efficiency is calculated by

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Term	Explanation
	summing the energetic efficiencies of all reactions involved at the cathode and the anode.
Energy requirement	The amount of energy per mole or per mass of product needed to drive an electrochemical conversion (including the energy needed in excess of the thermodynamic minimum required), also accounting for parasitic reactions (e.g., hydrogen evolution at the cathode, oxygen evolution at the anode).
Faradaic efficiency	In electrochemistry the efficiency with which electrons that are introduced into the reaction are converted into a specific product. Typically expressed as a percentage.
Fundamental research	A stage of commercialization where fundamental principles of a scientific or engineering process are observed and reported, and a technology concept is formed.
Gaseous carbon waste streams	Carbon dioxide, methane, or biogas that is present in a waste gas stream.
Life-cycle assessment	A technique used to catalog energy, water, and materials (e.g., chemicals, metals) inputs, outputs, and emissions over the life cycle of a process or product.
Long-lived	Carbon waste is not emitted through use of the product for a period of more than 100 years.
Low or zero carbon	A property of a process which describes the emissions attributed to the process. Low carbon means producing fewer carbon compounds such as carbon dioxide that might contribute to pollution than similar technologies. Zero carbon means the process is not associated with net emission of carbon wastes to the atmosphere. The terms carbon free, low carbon, carbon neutral are each synonymous with the spectrum of properties described as low or zero carbon.

Term	Explanation
Mineral carbonation	Formation of carbonates by contacting alkaline solids, often in an aqueous suspension, with carbon dioxide in a fluid state. In the context of this study, mineral carbonation refers to forming a useful product, rather than related chemical processes to sequester carbon in the form of natural carbonates.
Overpotential	In electrochemistry the difference in potential between the thermodynamically determined reduction potential of a half-reaction and the potential at which the half-reaction is observed experimentally.
Pilot scale	A stage of commercialization where a system validated in a relevant environment and at an engineering scale.
Selectivity	The amount of the converted starting material which forms the desired product. Typically expressed as a percentage and defined as selectivity = (amount of product)/(amount of conversion of starting material) * 100.
Sequestration	Carbon dioxide trapped for more than 100 years.
Short-lived	Carbon waste is emitted through use or disposal of the product in less than 100 years.
Storage	Carbon dioxide trapped for 100 years or less.
Technoeconomic analysis	A tool that is widely used in industry to evaluate commercial viability of any new technology.
Turnover frequency (TOF)	In a catalytic reaction the number of moles of product produced per mole of catalyst per unit of time.
Turnover number (TON)	In a catalytic reaction the number of moles of product produced per mole of catalyst.

Appendix B

Committee and Staff Biosketches

COMMITTEE

DAVID T. ALLEN (CHAIR), NAE, University of Texas, Austin

DR. DAVID T. ALLEN (NAE) is the Gertz Regents Professor of Chemical Engineering, and the Director of the Center for Energy and Environmental Resources, at the University of Texas at Austin. He is the author of seven books and over 250 papers, primarily in the areas of urban air quality, the engineering of sustainable systems, and the development of materials for environmental and engineering education. Dr. Allen has been a lead investigator for multiple air quality measurement studies, which have had a substantial impact on the direction of air quality policies. He directs the Air Quality Research Program for the State of Texas, and he is the founding Editor-in-Chief of the American Chemical Society's journal *ACS Sustainable Chemistry & Engineering*. The quality of his work has been recognized by the National Science Foundation, the AT&T Foundation, the American Institute of Chemical Engineers, the Association of Environmental Engineering and Science Professors, and the State of Texas. He has served on a variety of governmental advisory panels and from 2012 to 2015 chaired the U.S. Environmental Protection Agency's Science Advisory Board. Dr. Allen received his B.S. degree in chemical engineering, with distinction, from Cornell University in 1979. His M.S. and Ph.D. degrees in chemical engineering were awarded by the California Institute of Technology in 1981 and 1983. He has held visiting faculty appointments at the California Institute of Technology, the University of California, Santa Barbara, and the Department of Energy.

MARK A. BARTEAU, NAE, Texas A&M University

DR. MARK A. BARTEAU (NAE) is the vice president for research at Texas A&M University. Previously, Dr. Barteau served as Director of the University of Michigan Energy Institute and the inaugural DTE Energy Professor of Advanced Energy Research. He was elected to the National Academy of Engineering in 2006. Dr. Barteau brings extensive experience as a researcher, inventor, academic leader, and consultant for both U.S. and international organizations. His research focuses on chemical reactions at solid surfaces and their applications in heterogeneous catalysis and energy processes. His research has been funded by the National Science Foundation, the Department of Energy, the Air Force Office of Scientific Research, and NASA. Mark received

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his master's and Ph.D. in chemical engineering from Stanford University in 1977 and 1981, respectively.

MICHAEL BURKART, University of California, San Diego

DR. MICHAEL BURKART is currently a professor and Vice Chair of the Chemistry and Biochemistry Department at the University of California, San Diego, and Associate Director of the California Center for Algae Biotechnology. His research includes natural product synthesis, biosynthesis, and synthetic biology. He has broad experience in renewable fuels, chemicals, and materials. Dr. Burkart's laboratory pursues interdisciplinary research in the fields of bioorganic and synthetic organic chemistry and chemical biology. The laboratory is currently involved in the study of algal metabolic pathways with an emphasis on engineering improved biofuel production. Dr. Burkart received his B.A. in chemistry from Rice University in 1994 and his Ph.D. in organic chemistry from Scripps Research Institute in 1999.

JENNIFER DUNN, Northwestern University & Argonne National Laboratory

DR. JENNIFER DUNN is the Director of Research of the Northwestern-Argonne Institute of Science and Engineering and a Principal Environmental Analyst at Argonne National Laboratory. She is a research associate professor at Northwestern University in chemical and biological engineering. Jennifer investigates life-cycle energy consumption and environmental impacts of advanced transportation and fuel technologies, including biofuels and battery-powered electric drive vehicles. In previous work, Jennifer led life-cycle analysis projects in the United States for URS Corporation and supported mobile source emission reduction programs at the U.S. Environmental Protection Agency. She holds a Ph.D. in chemical engineering from the University of Michigan.

ANNE M. GAFFNEY, Idaho National Laboratory

DR. ANNE M. GAFFNEY is the director and laboratory fellow of the Process Science & Technology Division of Idaho National Laboratory. She received her doctorate in physical organic chemistry from the University of Delaware in 1981, and a bachelor's in chemistry and mathematics from Mount Holyoke College in 1976. Having worked at ARCO, DuPont, Rohm and Haas, and Lummus in various research and development (R&D) and leadership roles, she has been a most prolific inventor and an author with 247 patents or patent applications and 99 publications (plus two book chapters and two books edited), as well as 106 presentations or seminars. She has received many awards such as the ACS Award in Industrial Chemistry in 2013, ACS Fellow in 2010, the Tribute to Women in Industry Award in 2007, and the Catalysis Club of Philadelphia

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Award in 1999. Anne's most recent accomplishment is being the recipient of the 2015 Eugene J. Houdry Award of the North American Catalysis Society.

RAGHUBIR GUPTA, Susteon, Inc.

DR. RAGHUBIR GUPTA is President of Susteon, Inc. as of early 2018. Previously, Dr. Gupta served as the Senior Vice President of the Energy Technology Division at RTI International. Dr. Gupta obtained his B.Tech. degree in chemical engineering from the Indian Institute of Technology, New Delhi, India, and his Ph.D., also in chemical engineering, from the Illinois Institute of Technology, Chicago. Dr. Gupta's technical expertise ranges from coal/biomass gasification, synthesis gas (syngas) cleanup and utilization, syngas conversion into fuels and chemicals including Fischer-Tropsch chemistry, hydrogen production and storage, carbon capture, utilization, and sequestration, desulfurization of hydrocarbon fuels, production of cellulosic biofuels, and industrial water reuse. Dr. Gupta has presented his research work in a number of national and international conferences, published in a number of reputed journals, including a paper in *Science*, and holds more than 20 U.S. and foreign patents. Dr. Gupta is also a visiting research fellow at the Lenfest Center for Sustainable Energy at Columbia University in New York.

NILAY HAZARI, Yale University

DR. NILAY HAZARI is currently a professor of chemistry at Yale University. He received a B.Sc. (2002), majoring in chemistry, and a M.Sc. (2003) in inorganic chemistry working with Professor Leslie D. Field at the University of Sydney. He then completed a D. Phil in inorganic chemistry (2006) at the University of Oxford as a Rhodes Scholar. In 2009 he started his independent career at Yale. His primary research focus is the mechanism-based design of homogeneous transition-metal catalysts for the synthesis of fine and commodity chemicals. A growing interest involves the design and synthesis of small molecules for use in photovoltaics. His approach to developing new catalysts involves detailed experimental and theoretical studies of reaction mechanisms. To date his group has developed state-of-the-art catalysts for the hydrogenation of carbon dioxide to formic acid, the dehydrogenation of formic acid and methanol to carbon dioxide and hydrogen, and palladium- and nickel-catalyzed cross-coupling. His precatalysts for palladium-catalyzed cross-coupling are commercially available from a number of companies on both research (gram) and industrial (kilogram) scales. Professor Hazari has received a number of awards including the American Chemical Society Harry Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator (2017), the Arthur Greer Memorial Prize for Outstanding Scholarship by Junior Faculty Members in the Social Sciences and Sciences at Yale University (2015), the Camille and Henry Dreyfus Teacher Scholar Award (2014), and the National Science Foundation Career Award (2012). In 2013 he was named an Alfred P. Sloan Research Fellow and in 2012 an Organometallics Fellow from the American Chemical Society Journal *Organometallics*.

MATTHEW KANAN, Stanford University

DR. MATTHEW KANAN is an associate professor of chemistry at Stanford University. Dr. Kanan develops new catalysts and chemical reactions for applications in renewable energy conversion and CO_2 utilization. His group at Stanford University has recently developed a novel method to create plastic from carbon dioxide and inedible plant material rather than petroleum products and pioneered the study of "defect-rich" heterogeneous electrocatalysts for converting carbon dioxide and carbon monoxide to liquid fuel. Dr. Kanan completed undergraduate study in chemistry at Rice University (B.A. 2000 Summa Cum Laude, Phi Beta Kappa). During doctoral research in organic chemistry at Harvard University (Ph.D. 2005), he developed a novel method for using DNA to discover new chemical reactions. He then moved into inorganic chemistry for his postdoctoral studies as a National Institutes of Health Postdoctoral Research Fellow at the Massachusetts Institute of Technology, where he discovered a water oxidation catalyst that operates in neutral water. He joined the Stanford Chemistry Department faculty in 2009 to continue research into energy-related catalysis and reactions. His research and teaching have already been recognized in selection as one of *Chemistry & Engineering News*' first annual Talented 12, the Camille Dreyfus Teacher-Scholar Award, Eli Lilly New Faculty Award, and recognition as a Camille and Henry Dreyfus Environmental Mentor, among other honors. The Kanan Lab addresses fundamental challenges in catalysis and synthesis with an emphasis on enabling new technologies for scalable CO_2 utilization. The interdisciplinary effort spans organic synthesis, materials chemistry, and electrochemistry.

PAUL KENIS, University of Illinois at Urbana-Champaign

DR. PAUL J.A. KENIS is the William H. & Janet G. Lycan Professor and Head of the Chemical and Biomolecular Engineering Department at the University of Illinois at Urbana-Champaign. Dr. Kenis received his B.S. in chemistry from Nijmegen-Radboud University (1993) and his Ph.D. in chemical engineering from Twente University in the Netherlands. He was a postdoctoral research fellow at Harvard University (1997-2000), where his research focused on microfluidics. In 2000 Dr. Kenis started his independent research position as an assistant professor in the Department of Chemical Engineering at the University of Illinois at Urbana-Champaign. His research program focuses on developing microchemical systems for applications in energy and biology. Presently his efforts focus on electrolysis of CO_2 to value-added chemicals, continuous flow microreactors for semiconductor nanoparticle synthesis, microfluidic lung-on-chip platforms, and solid form screening for pharmaceutical formulation. Prior efforts included microfuel cells, microreactors for radiolabeling of biomolecules, and microfluidic platforms for protein crystallization and cell biology studies. His research has been recognized through a 3M young faculty award, an NSF CAREER award, a Xerox Award, as well as best paper awards from the Separations Division of AICHE and the Society for Experimental Biology & Medicine.

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HOWARD KLEE, World Business Council for Sustainable Development, retired

DR. HOWARD KLEE currently manages an independent consulting practice based in Geneva, Switzerland, focused on sustainable business practices, programs, and management. Dr. Klee previously worked with Chevron and Amoco-BP before joining the World Business Council for Sustainable Development (WBCSD) in 2000. He has served in a number of executive and business functions, including strategic planning, program management, business development, environmental affairs, and manufacturing. Dr. Klee received his undergraduate degree in chemistry from Williams College (1967), and his doctorate in chemical engineering from the Massachusetts Institute of Technology (1972). He also completed an executive management program at Northwestern University's Kellogg Business School (1997). He previously served on President Clinton's Council on Sustainable Development, and as a Director for the Foundation for Research on Economics and the Environment. He has held adjunct teaching positions at the University of California (Davis), the University of Michigan, and the University of Geneva, where he has developed and taught courses in engineering design, technical communications, business, and the environment. From 2000 until 2011, Dr. Klee developed and served as Program Director for "The Cement Sustainability Initiative" (CSI) at WBCSD. This program is part of a long-range change management initiative for the cement industry as it reduces its environmental footprint and product impacts, while improving the benefits realized from its activities. Twenty-four geographically diverse companies, eight industry trade organizations, and several partners participate in this global program. The effort is now widely recognized as a leading example of results that can be achieved through voluntary business action to address key sustainability issues. For many years he also directed the WBCSD's Tire Industry Project and helped manage WBCSD's activities in China. Since 2013 Dr. Klee has done independent consulting and/or advisory work for the World Business Council, Cement Business Advisory, the Institute of Industrial Productivity, and private-sector clients. Today he is widely recognized for his expertise on sustainability issues in the cement sector. He currently divides his time between Switzerland and California. Dr. Klee also has an active career as an artist, with his paintings held in private collections in Switzerland, France, and the United States.

GAURAV N. SANT, University of California, Los Angeles

DR. GAURAV N. SANT is an associate professor and a Henry Samueli Fellow at the University of California, Los Angeles (UCLA), where he is also the Director of the Institute for Carbon Management. Dr. Sant's research interests include reactions at solid-liquid-vapor interfaces including dissolution, precipitation, and electrochemical corrosion with applications to (i) cement, concrete, and porous media; (ii) biological tissues; (iii) metals and alloys; (iv) natural and synthetic minerals; and (v) glasses. In his research, focus is placed on understanding the mechanistic origins of formation, degradation, and aging of such materials in environments of relevance to engineered, biological, and geological systems. The outcomes of this work are described in more than 100

refereed journal publications. Dr. Sant also leads Carbon Upcycling UCLA / CO_2Concrete: a precommercial venture based at UCLA that was recently selected as a finalist in the NRG COSIA Carbon XPRIZE Competition. Dr. Sant's research has been recognized by numerous awards, including the National Science Foundation's CAREER Award, a Hellmann Fellowship, RILEM's Gustavo Collonnetti Medal, the American Concrete Institute's Walter P. Murphy Jr. and J.C Roumain Awards, and selection as one of UCLA's Optimists. Dr. Sant received his B.S., M.S. and Ph.D. in civil engineering from Purdue University in 2006, 2007, and 2009, respectively.

CATHY L. TWAY, The Dow Chemical Company

DR. CATHY L. TWAY is the Director for the Materials Science and Engineering Capability of Core Research & Development. In this role, Cathy is responsible for a global team of scientists and engineers specializing in materials science, processing technologies, engineering design, and numerical modeling for predictive engineering. Cathy joined Dow in 2007 as a Research Leader in the Inorganic Chemistry and Catalysis organization, where she developed and led the Core R&D efforts for catalyst discovery and also introduced several new inorganic materials research programs. Most recently, Cathy was the Director of the Inorganic Materials and Heterogeneous Catalysis Capability within Core R&D, where she was responsible for expanding research capabilities in heterogeneous catalysis, inorganic materials, and characterization. Prior to joining Dow, Cathy held positions at Celanese, Solutia, and AkzoNobel, holding both individual contributor and R&D leadership roles. Her industrial experience covers the entire catalyst project life cycle including front-end identification and creation of new technologies, process scale-up, commercialization, and plant support. Over her career, Cathy has commercialized two inorganic materials and four catalyst technologies, with two of these processes still in use today. Cathy earned her B.S. degree in chemistry from Wichita State University and her Ph.D. in physical inorganic chemistry from the University of Nebraska–Lincoln.

STAFF

DAVID M. ALLEN, Senior Program Officer

David Allen is a Senior Program Officer for the National Academies' Board on Atmospheric Sciences and Climate (BASC). From 2003 to 2015, David worked at the United States Global Change Research Program (USGCRP) Office where he focused on international global change research and international assessment. In this role, he focused on developing and maintaining a comprehensive international portfolio for the USGCRP. Examples of some of the activities include national funding of international research programs (e.g., World Climate Research Programme, Future Earth), recruiting and conducting national reviews of international assessments (Intergovernmental Panel on Climate Change, World Ocean Assessment), coordinating an interagency international working group, and coordinating funding for regional global change research and capacity building organizations (Inter-American Institute for Global Change Research, Asia-Pacific Network for Global Change Research, and the SyTem for Analysis, Research and Training). David received his B.A. in sociology and premedical sciences from the University of Massachusetts at Boston and his M.S. in biological oceanography from the University of Washington.

CAMLY TRAN, Senior Program Officer

Camly joined the Board on Chemical Sciences and Technology at the National Academies of Sciences, Engineering, and Medicine in 2014 as a postdoctoral fellow. During her short time at the Academies, she has led and supported more than ten consensus studies and workshops focused at the intersection of chemistry and policy in four main areas: education, workforce, defense, and research. As a Senior Program Officer, she is currently leading a study on advancing separations science in the United States, supporting the activities of the Chemical Sciences Roundtable, and co-leading an Academies-wide transformation effort on workforce. She received her Ph.D. in bioinorganic chemistry from the Department of Chemistry at Brown University and her B.S. degree in chemistry from Carnegie Mellon University.

ELIZABETH (BETH) ZEITLER, Senior Program Officer

Beth is a globally experienced energy and transportation analyst, providing science-informed, actionable advice to private- and public-sector decision makers. As a Senior Program Officer of the National Academies of Sciences, Engineering, and Medicine, she leads studies on key areas of domestic and global energy policy. She has supported studies on vehicle technologies, electric vehicle deployment, and energy resource potential on Department of Energy lands. She is currently leading a study on light-duty vehicle fuel economy technologies and supporting studies of carbon

utilization and data science for urban sustainability. Trained as a chemist, Beth earned her Ph.D. from Princeton University in 2014, where she examined electrochemical reactions for carbon dioxide reduction. After completing her Ph.D., Beth initiated her energy and transportation policy work as a Christine Mirzayan Fellow of the Board on Energy and Environmental Systems at the National Academies. To understand how the growing world is being built, from 2015 to 2017 Beth served as a data advisor and AAAS Science and Technology Policy Fellow at the Millennium Challenge Corporation, a U.S. foreign assistance agency.

ERIN MARKOVICH, Senior Program Assistant/Research Assistant

Erin Markovich is currently a senior program assistant and research assistant with the Board on Atmospheric Science and Climate (BASC) and the Polar Research Board (PRB) at the National Academies. She was born and raised in Naperville, Illinois, a southwest suburb of Chicago. In May 2015, she earned a bachelor's degree in atmospheric sciences from the University of Illinois at Urbana-Champaign and in August of that year, she moved to Washington, DC, to work for the National Academies. Erin has been a staff member of BASC and PRB since then and has provided support to numerous studies in an administrative capacity. Erin remains connected to the atmospheric science community by staying involved in the American Meteorological Society and furthers her education both formally and informally through coursework and literature readings.

ANNA SBEREGAEVA, Associate Program Officer

Anna Sberegaeva joined the Academies in 2016 as an Associate Program Officer of the Board on Chemical Sciences and Technology. Prior to that she was a recipient of the American Society for Engineering Education Fellowship and held the position of a postdoctoral research associate at the Naval Research Laboratory. Anna earned her Ph.D. in organometallic chemistry from the University of Maryland College Park and her M.S. degree in inorganic chemistry from the University of Florida. Anna graduated with a B.S. (chemistry) and a B.A. (linguistics) degree from the Herzen State Pedagogical University in St. Petersburg, Russia.