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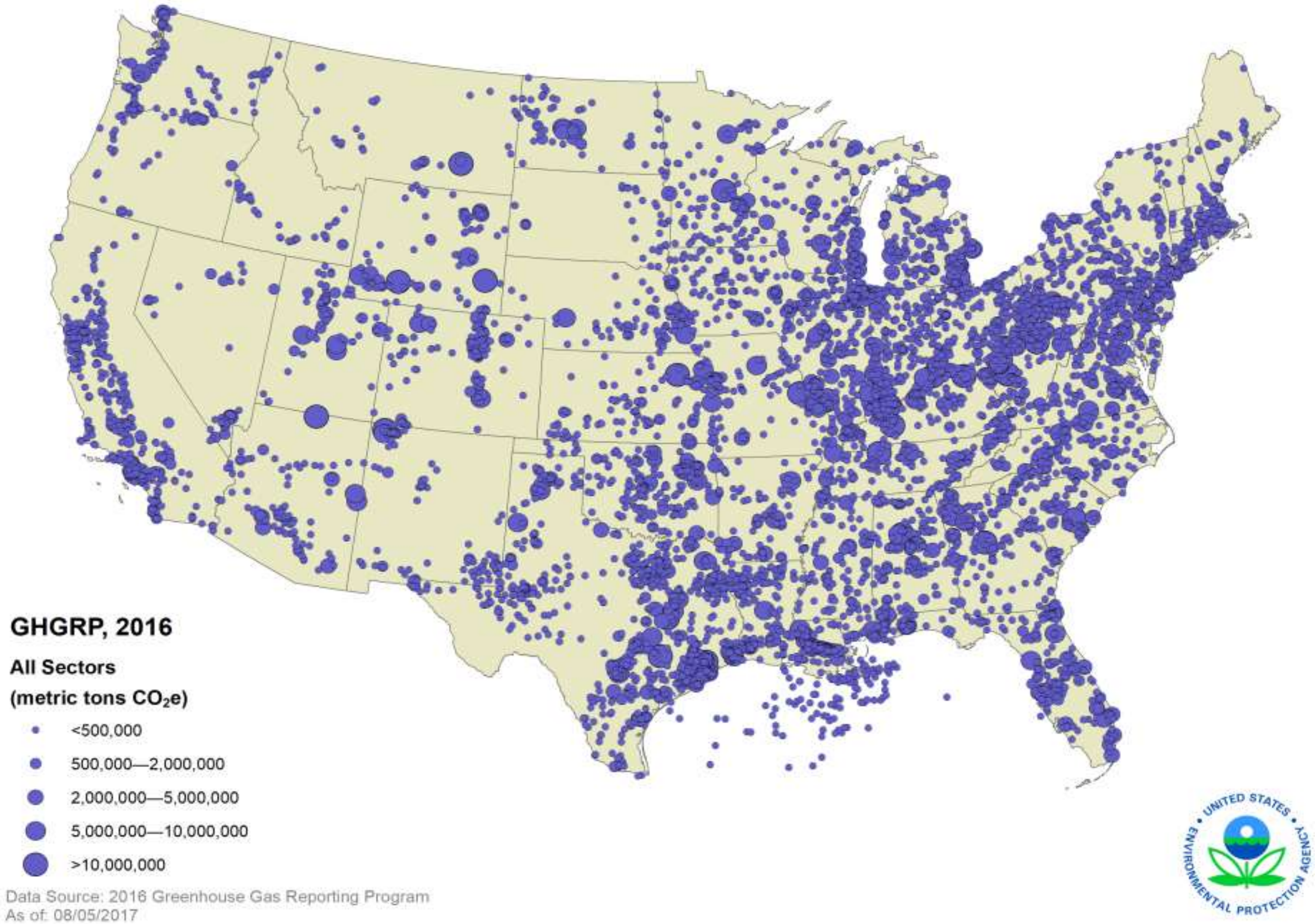
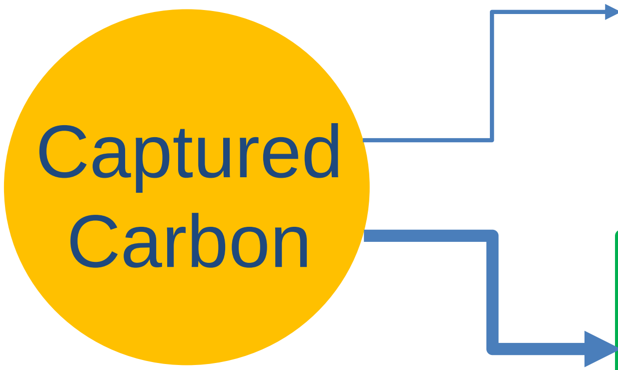
Gaseous Carbon Waste Streams Utilization: Status and Research Needs

Michael D. Burkart (Member)
University of California, San Diego

The study is motivated by an interest in increasing carbon waste gas utilization.



Carbon waste gas utilization is part of a carbon capture, utilization and sequestration (CCUS) system.



Sequestered: Captured carbon may be disposed of thousands of feet underground where it can remain permanently trapped (see also sister study: *Carbon Dioxide Removal and Reliable Sequestration, RSO- Katie Thomas, http://nas-sites.org/dels/studies/cdr/).*

Utilized: CO_2, CH_4 and biogas may be used as a feedstock for products that have market value, such as fuels, building materials, plastics or other useful solids, chemicals or animal feed.

Carbon waste gases are captured at its point of production or from the atmosphere and may be separated from other byproducts, compressed and/or transported.

Statement of Task

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, bio-fuels 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 lifecycle 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.

Study Committee

David Allen, NAE (*Chair*), University of Texas, Austin
Mark Barteau, **NAE**, Texas A&M University
Michael Burkart, University of California, San Diego
Jennifer Dunn, Northwestern University/Argonne National Laboratory
Anne Gaffney, Idaho National Laboratory
Raghubir Gupta, Susteon Inc.

Nilay Hazari, Yale University
Matthew Kanan, Stanford University
Paul Kenis, University of Illinois, Urbana-Champaign
Howard Klee, World Business Council for Sustainable Development (retired)
Gaurav Sant, University of California, Los Angeles
Cathy Tway, The Dow Chemical Company

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Camly Tran, Study Director, Board on Chemical Sciences and Technology
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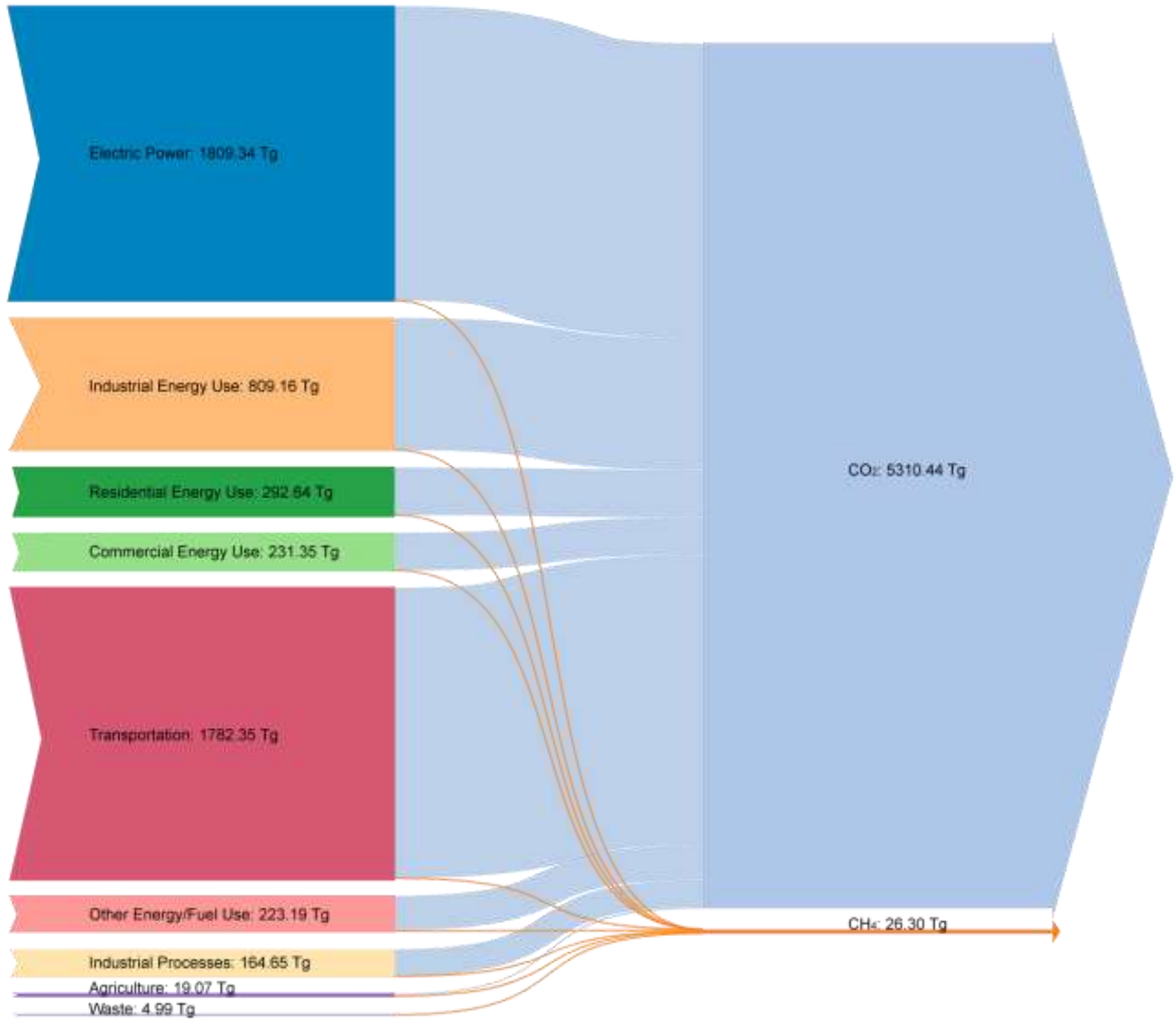
HAIBO ZHAI, Carnegie Mellon University

The review of this report was overseen by **John L. Anderson**, (NAE) Illinois Institute of Technology, and **Elisabeth M. Drake**, (NAE) Massachusetts Institute of Technology.

The committee gathered data from a variety of public sources over 11 months.

- **Committee Knowledge & Experience**
  - A group of experts with broad and varied experience in industrial and academic settings, and with expertise in chemical, biological and mineral transformations of carbon dioxide and methane, as well as life-cycle and technoeconomic analyses.
- **Data-gathering conducted at 4 committee meetings and 2 webinars**
  - Speakers and invited participants included individuals from government entities (DOE, ARPA-E, congressional staffers), researchers from universities, national labs, industry and other institutions, and several start-up and established companies utilizing carbon gases. Speakers and invited guests are listed in the report.
  - Information was sought on technology status, challenges and opportunities, as well as business, economic and life-cycle aspects of carbon waste use technologies.
- **Peer-reviewed research literature**
- **Community input through study website**

CO$_2$ is more abundant than methane, and has greater opportunities for utilization at large scale.



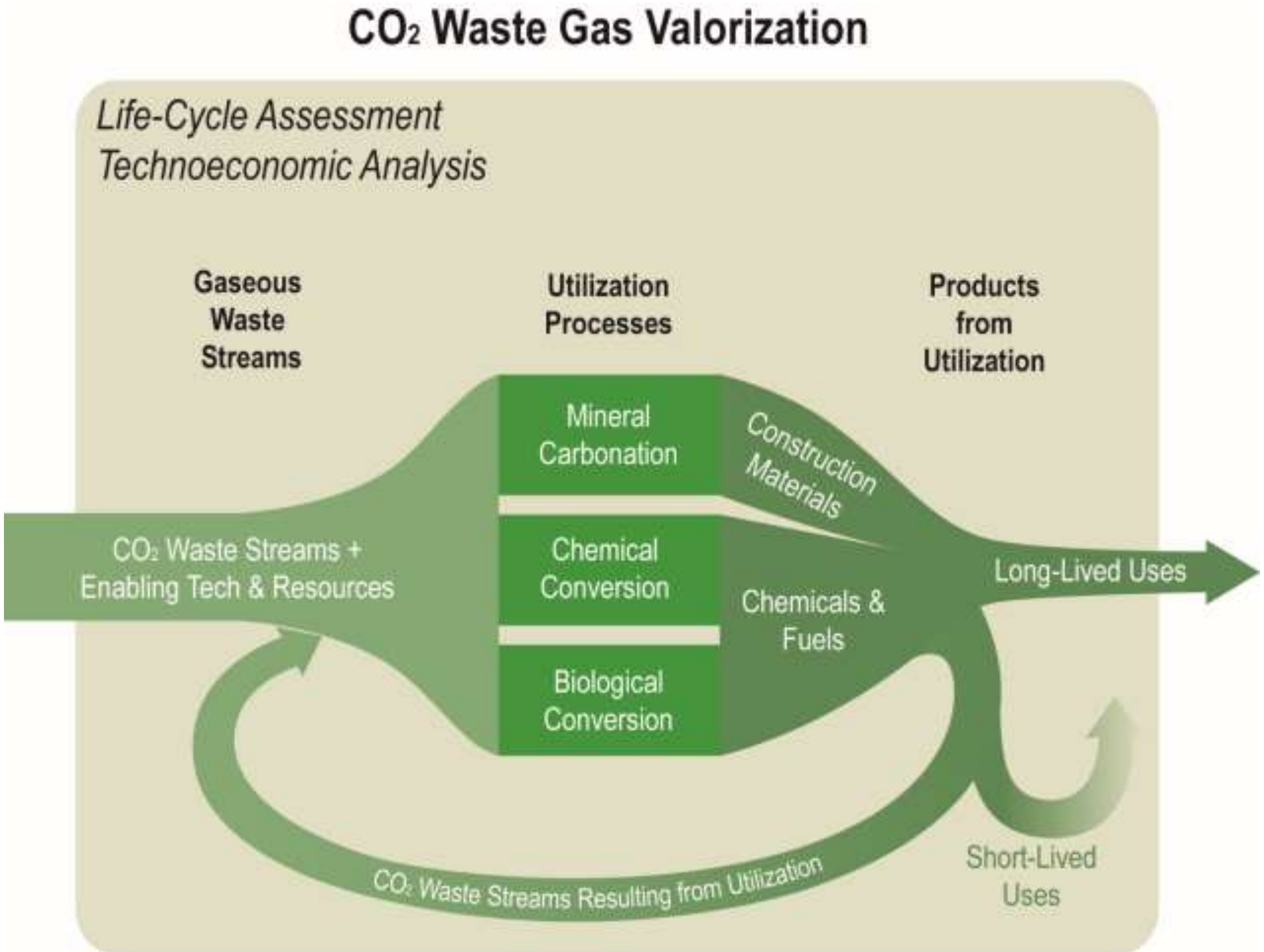
The committee considered research needs for CO_2 and methane waste gas utilization.

- CO_2 is more abundant than methane due to the larger number of sources and the larger volume of gas produced at individual sources.
- Methane is an energy-carrying molecule, so has greater incentives for capture and direct use as a fuel without chemical conversion, rather than utilization through chemical transformations.
- Because it is low energy, CO_2 has greater challenges in catalysis to make chemicals and fuels.
- Both methane and CO_2 waste gas sources face challenges with collection or capture, contamination removal and transportation; these challenges vary among waste gas streams.
- Because CO_2 has vastly greater volume and also greater challenges in chemical and biological utilization, it was the primary focus of the report and research agenda.

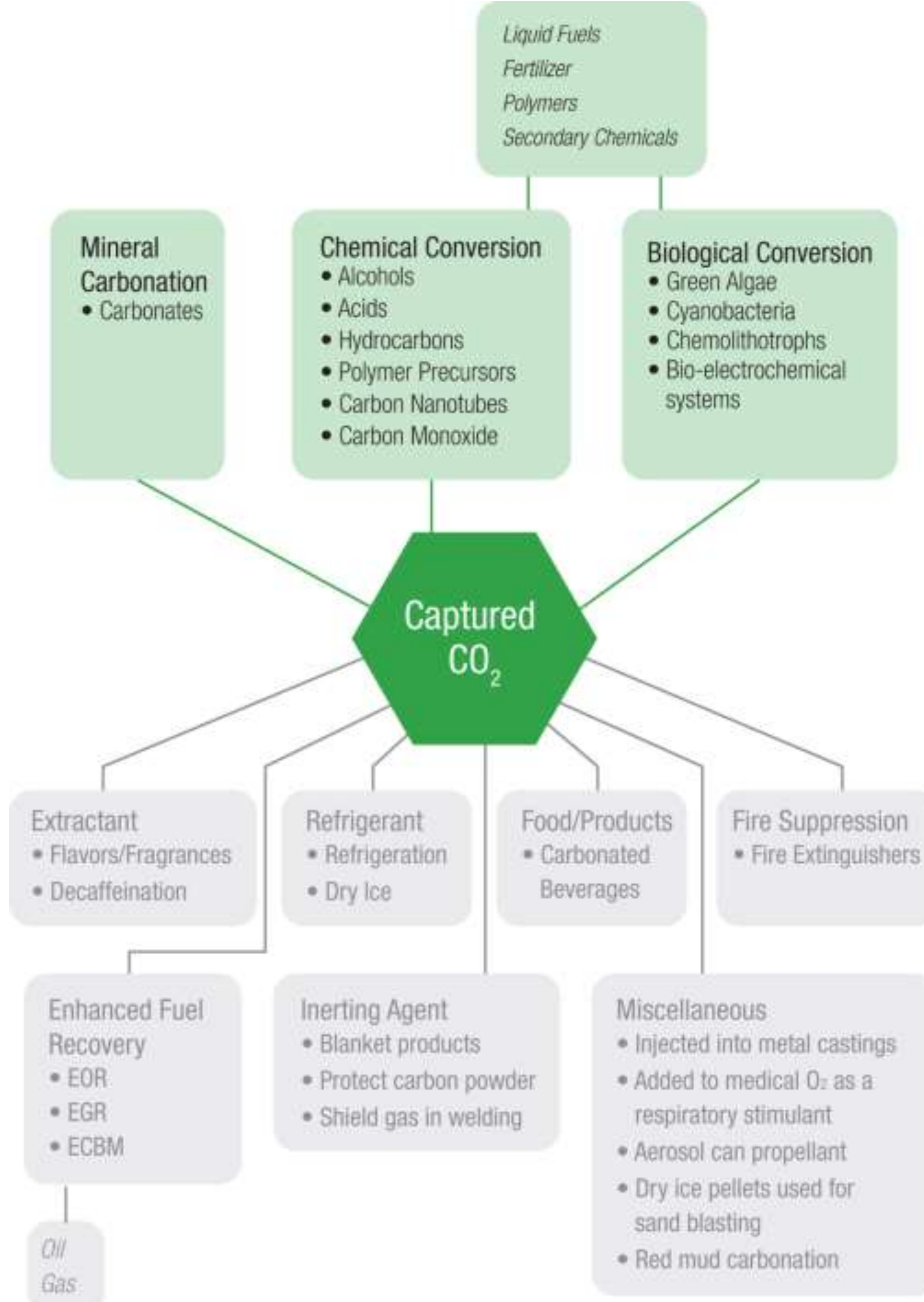
The committee organized the report around key features of the carbon utilization system.

- Carbon dioxide waste gases are generated in much higher volume, have fewer competing uses, and have many technical challenges to utilization.
- Carbon waste gas utilization follows three technical pathways.
  - Pathways for carbon dioxide utilization are mineral carbonation, chemical and biological conversion.
  - Methane utilization follows two pathways: chemical and biological conversion.
- Enabling technologies and resources, such as efficient separations and low-carbon sources of hydrogen and electricity, are key to realizing carbon utilization with net reduction in greenhouse gases released to the atmosphere.
- Life-cycle assessment and technoeconomic analysis are important evaluation tools for carbon utilization technologies.

Carbon Dioxide Utilization

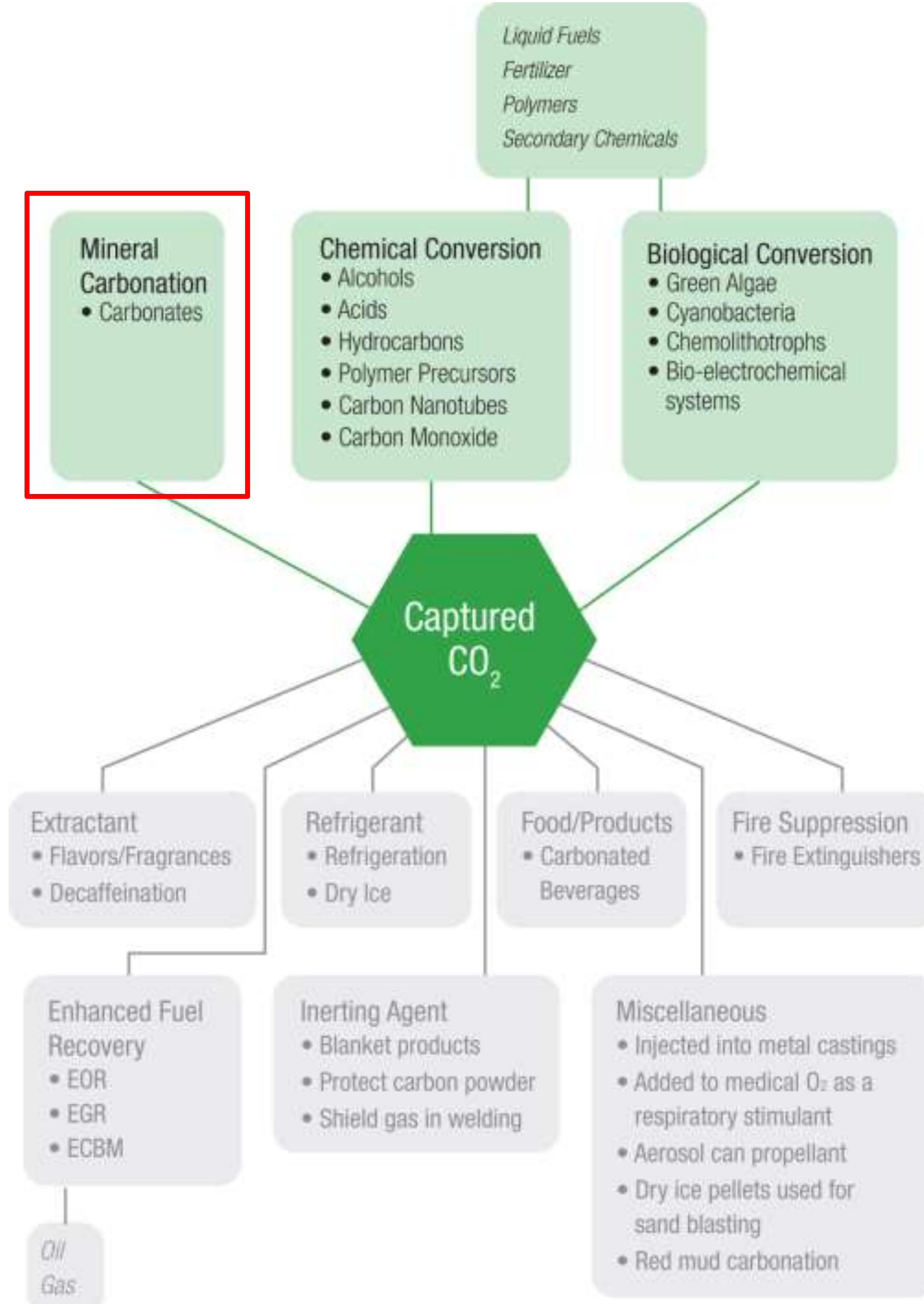


The report focused on three utilization pathways that results in chemical transformation of CO_2 into a valuable product.



Mineral carbonation processes

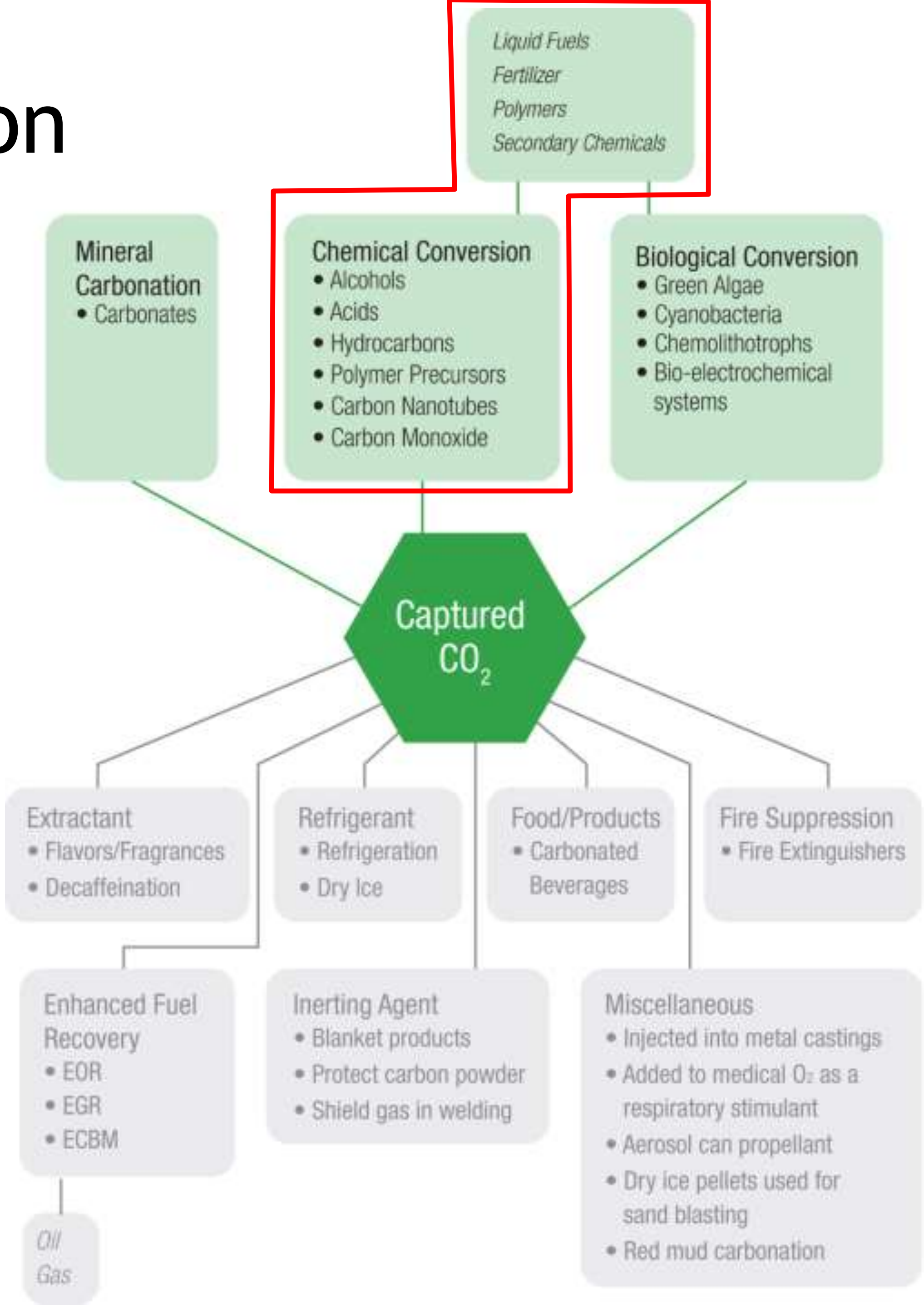
transform carbon dioxide into mineral carbonates, which can be used to make concrete and cement. Because billions of tons per year of these building materials are used and the products have lifetimes that span decades, mineral carbonation represents a significant opportunity for long-term carbon sequestration in addition to being an opportunity for carbon utilization.



Chemical utilization processes

transform carbon dioxide into carbon containing materials such as fuels, polymers, commodity chemicals, and fine chemicals.

Some processes that use waste carbon dioxide are already operating commercially, though current operations are generally dependent on locally available, low-cost, non-transportable energy resources or feedstocks, so they are not currently scalable in every location.



Biological utilization processes

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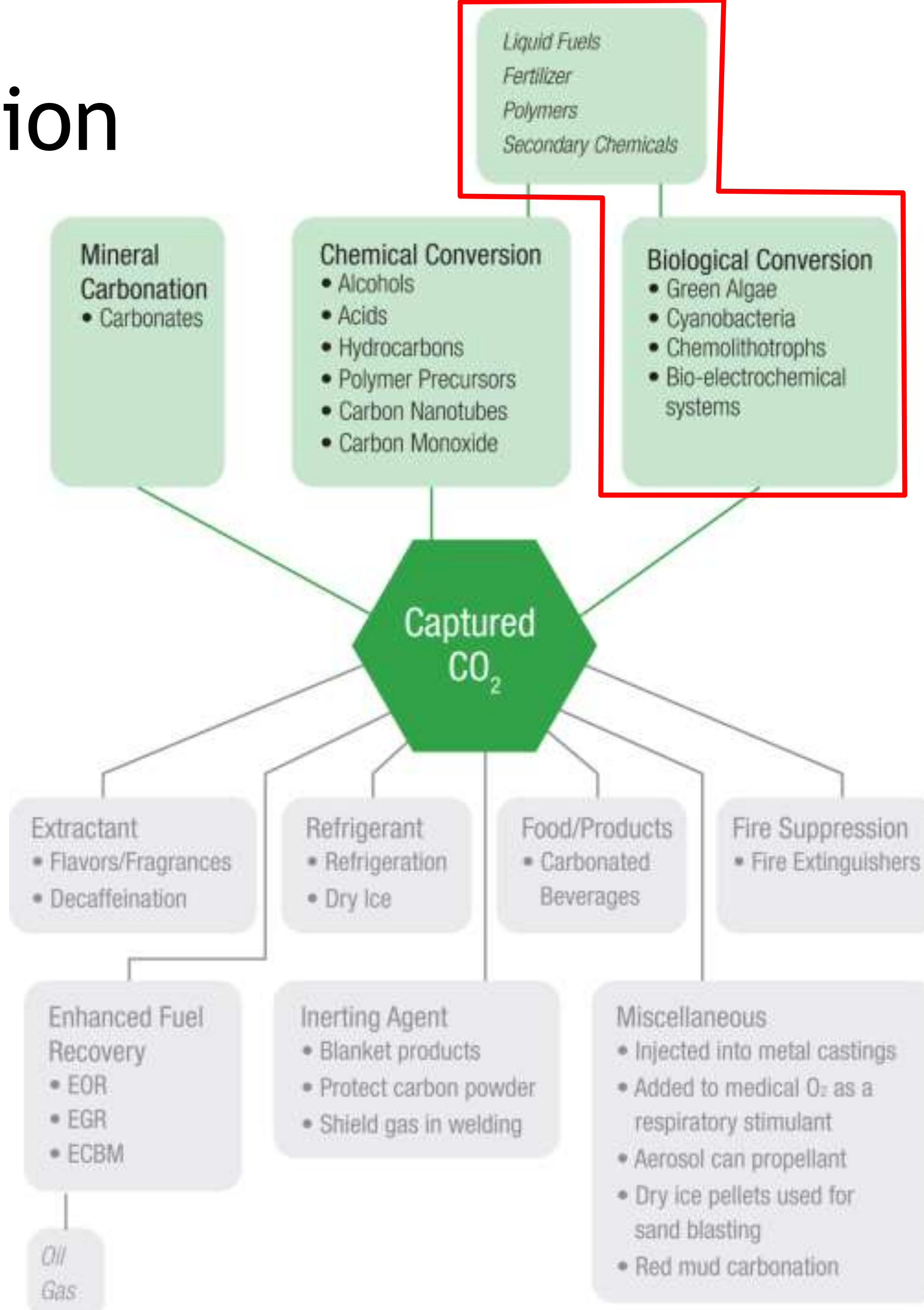
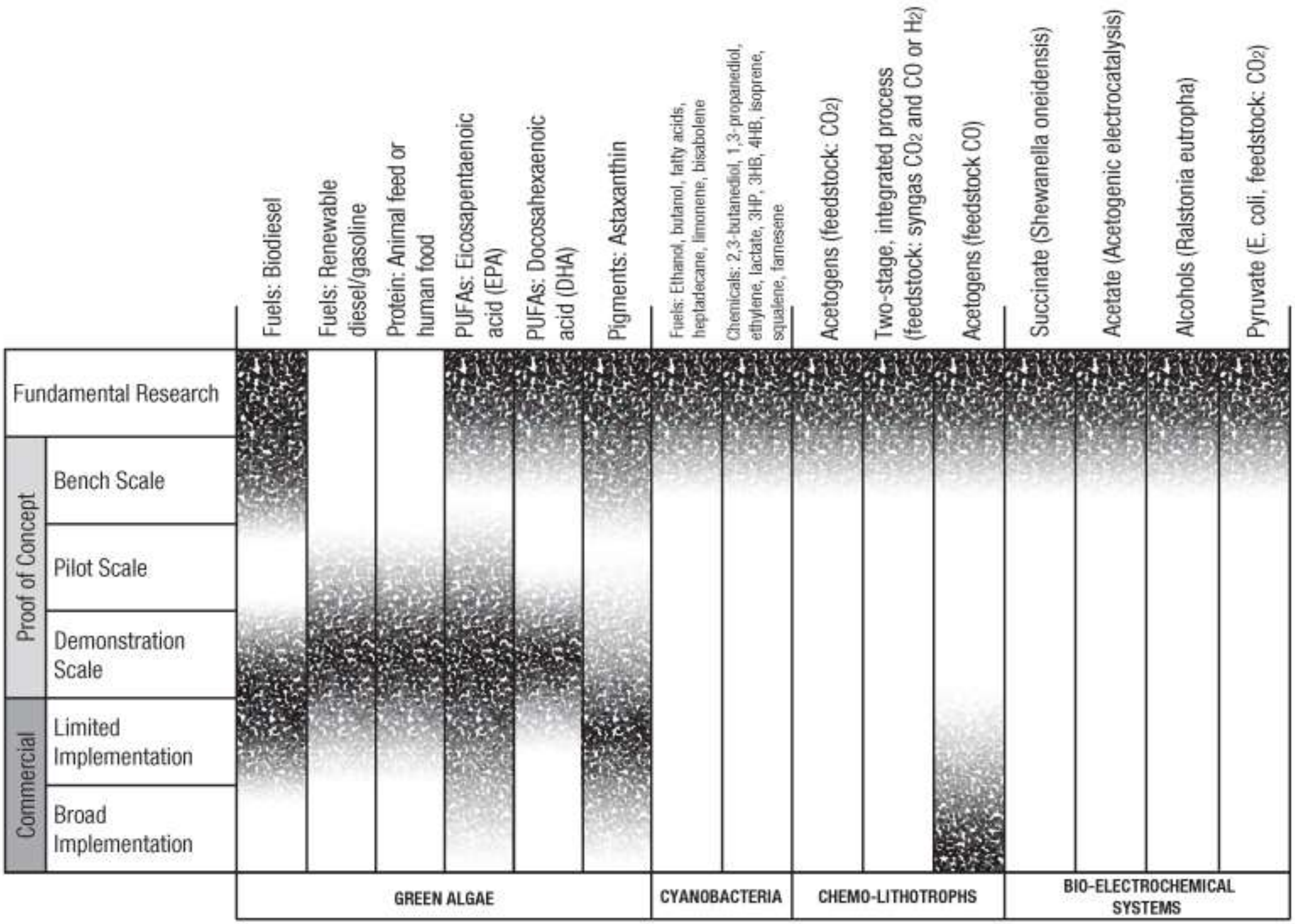


Biological Utilization



Biological Utilization – Key Barriers

Platform	Product	Key Barriers
Green Algae	**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	**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: CO_2)	Low degree of reduction
	Two-stage, integrated process (feedstock: syngas CO_2 and CO or H_2)	Hydrogen requirement, low productivity and titers, scale-up
	Acetogens (feedstock CO)	Scalability
Bioelectro-chemical systems	Succinate (Shewanella oneidensis)	Electrode surface, reactor design and operations improvements
	Acetate (Acetogenic electrocatalysis)	Product recovery, scalability
	Alcohols (Ralstonia eutropha)	Engineering organism to produce alcohols, produce formate under culturing conditions, and withstand electricity; scalability
	Pyruvate (E. coli, feedstock: CO_2)	Strain modifications, link to production of chemicals and fuels, scalability

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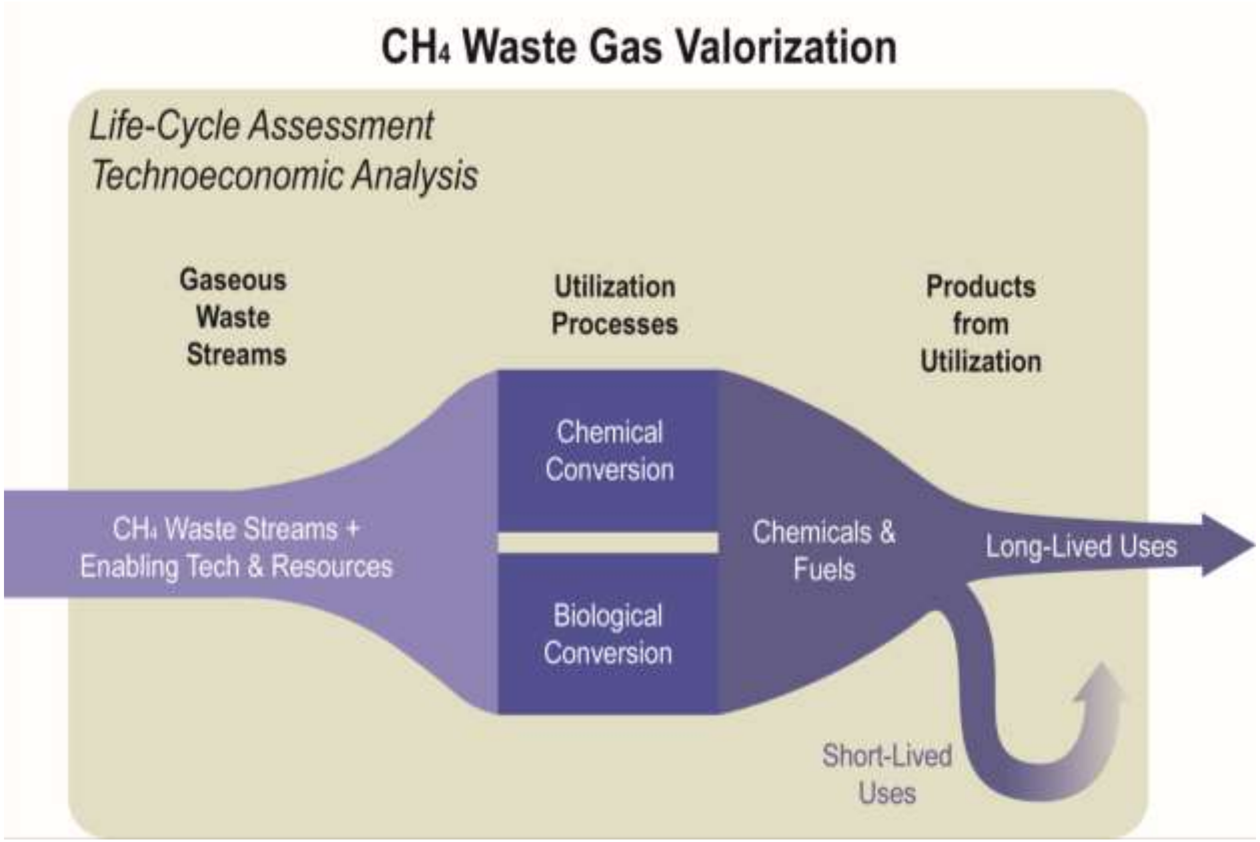
Biological Utilization Research Agenda

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 non-photosynthetic 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 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 non-photosynthetic organisms, including expansion of tools for genetic incorporation, selectable markers, promoter elements, protein folding and stability, and post-translational 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 non-traditional products and new products for unmet needs in commodity and specialty chemicals. This could expand the portfolio of products made via carbon utilization.

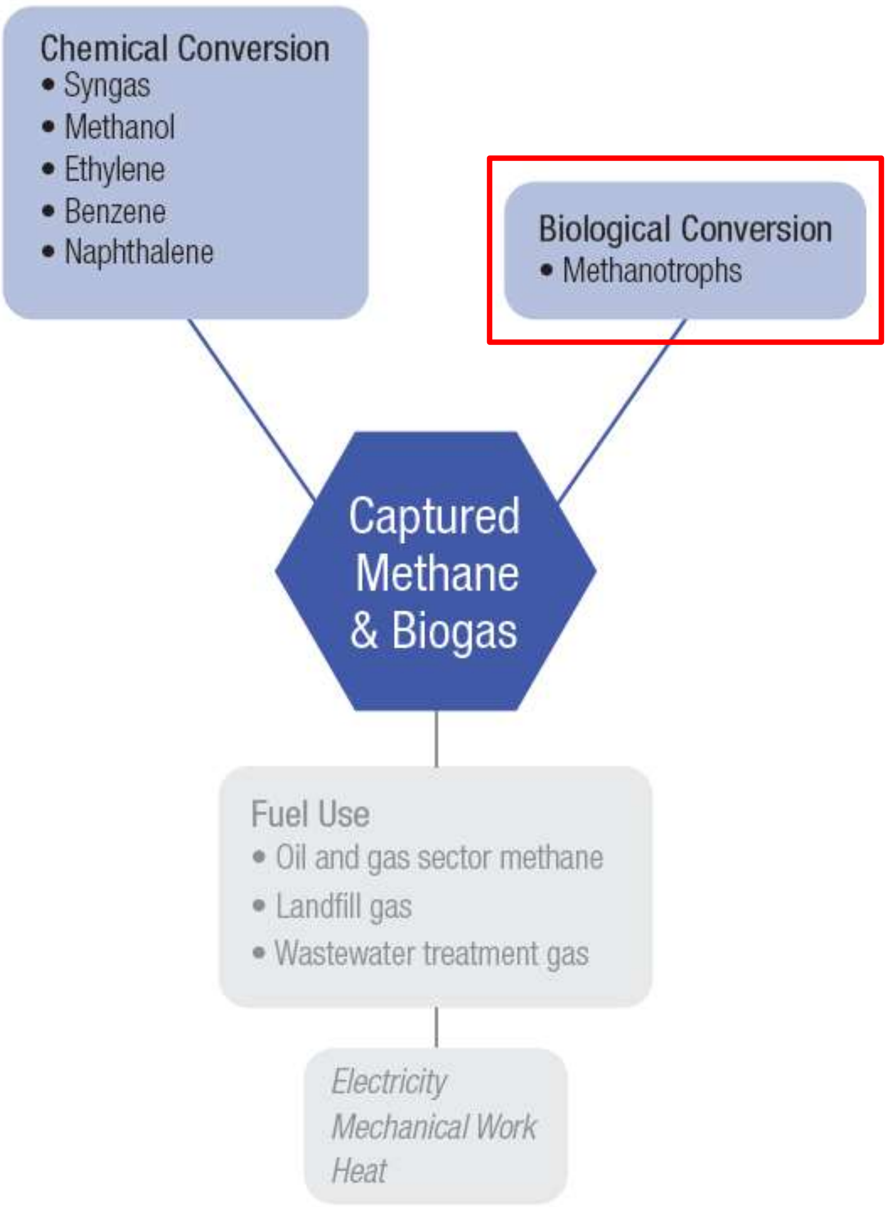
Methane and Biogas Utilization



Methane and biogas utilization processes

transform methane into carbon containing materials such as fuels, polymers, commodity chemicals, and fine chemicals.

Some processes that use waste methane or biogas are already operating commercially, although they must compete with fuel uses of methane.



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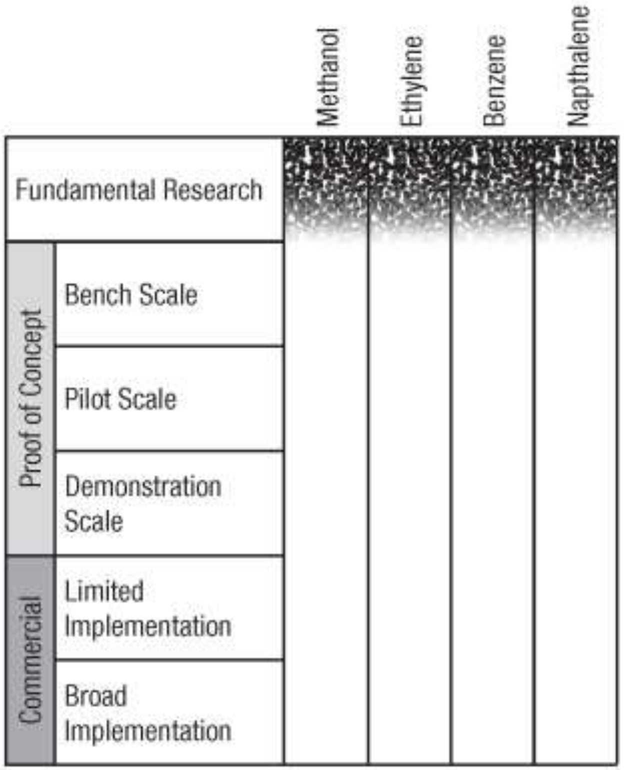
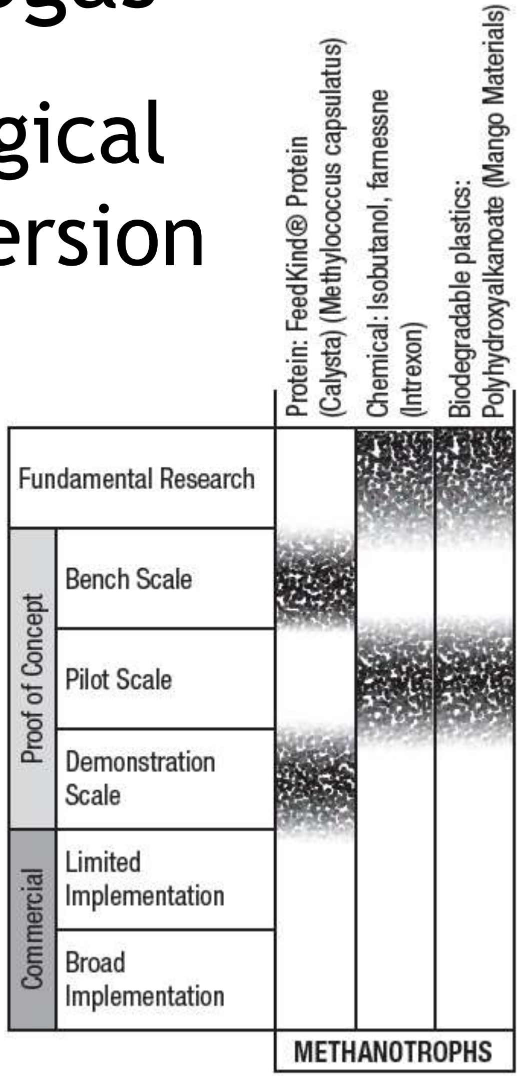
Methane and Biogas

chemical conversion

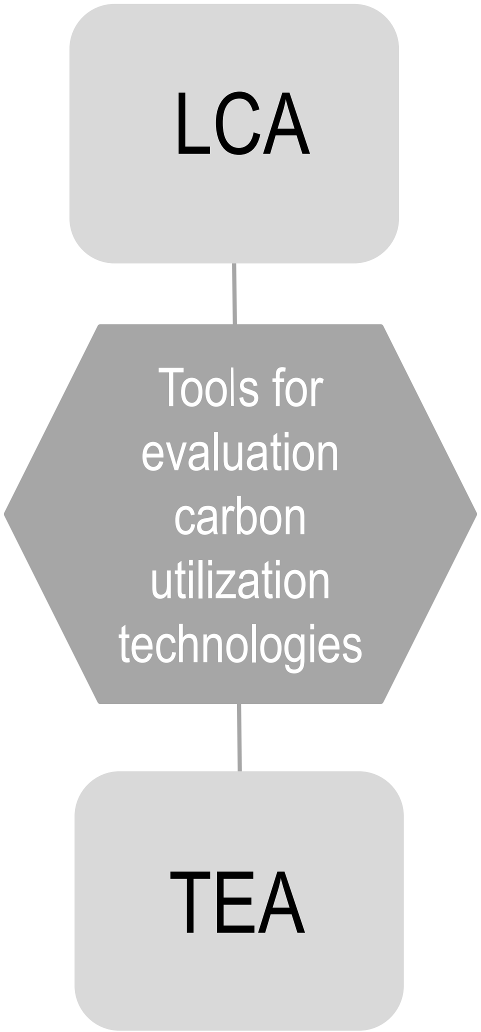


biological conversion



Life-cycle assessment and Technoeconomic analysis

- Critical tools that can be used to help evaluate carbon utilization technologies.
- LCA is used to evaluate the total energy requirements and environmental impacts involved in producing products from waste carbon feedstocks, and whether the process leads to a net reduction in greenhouse gas emissions.
- TEA is used to determine the technical and economic viability of a new technology.



The committee identified factors that may be used to assess commercial viability of carbon utilization technologies.

- Factors relevant to most technologies including CU
  - Economic value
  - Scale, market capacity and market penetration
  - Control of external factors associated with the technology
  - Unintended outcomes and consequences
- Factors especially relevant to CU technologies
  - Availability and suitability of waste stream
  - Risks associated with the use of waste as a feedstock
  - Life-cycle greenhouse gas reductions

Example criteria for evaluation of factors are shown below. Evaluators may weigh factors and criteria differently for different applications.

- 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 waste-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?

Example criteria for evaluation of factors are shown below. Evaluators may weigh factors and criteria differently for different applications.

- 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?

In practice, different evaluators may weigh the factors and criteria differently.

- The research agenda spans needs from fundamental research to commercial development.
  - It is not possible to evaluate every criterion when a technology is at the fundamental scale, but evaluating emerging technologies early in development will give the first indications of potential commercial viability.
  - As the technology progresses to pilot and demonstration scales, additional criteria can be addressed to evaluate its potential to move into the commercial arena.
- Each program or organization will have specific goals, which will result in different prioritization of factors and criteria in evaluating carbon utilization technologies.

The committee's recommendation is to implement the research agenda

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.

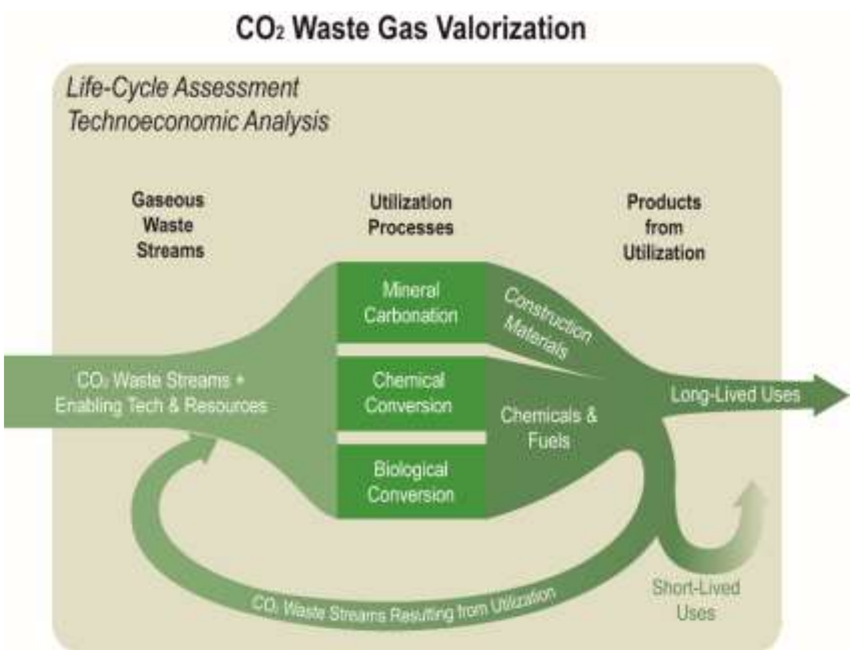
Specifically:

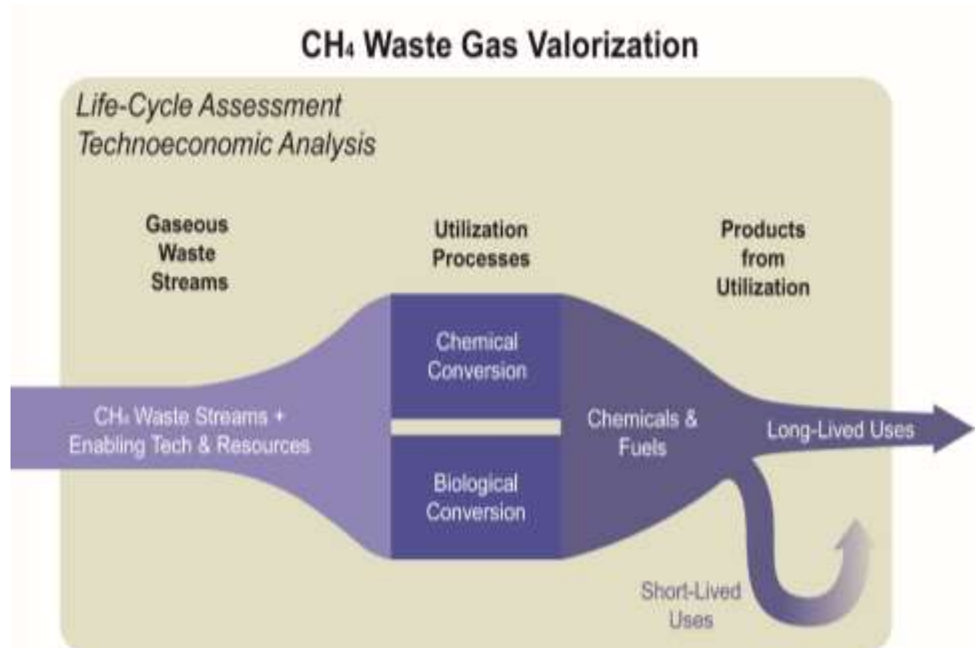
- The U.S. government and the private sector should support research and development in carbon utilization technologies to develop pathways for making valuable products and to remove technical barriers to waste stream utilization.
- The U.S. government and the private sector should support the development of new life-cycle assessment and techno-economic tools and benchmark assessments that will enable consistent and transparent evaluation of carbon utilization technologies.
- The U.S. government and the private sector should support 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 lifecycle reduction of greenhouse gas emissions.

The committee's recommendation is to implement the research agenda, coordinating with existing efforts in carbon utilization

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 sector. 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.

Final Thoughts: Carbon utilization is a system that requires multiple parallel advances to be successful.





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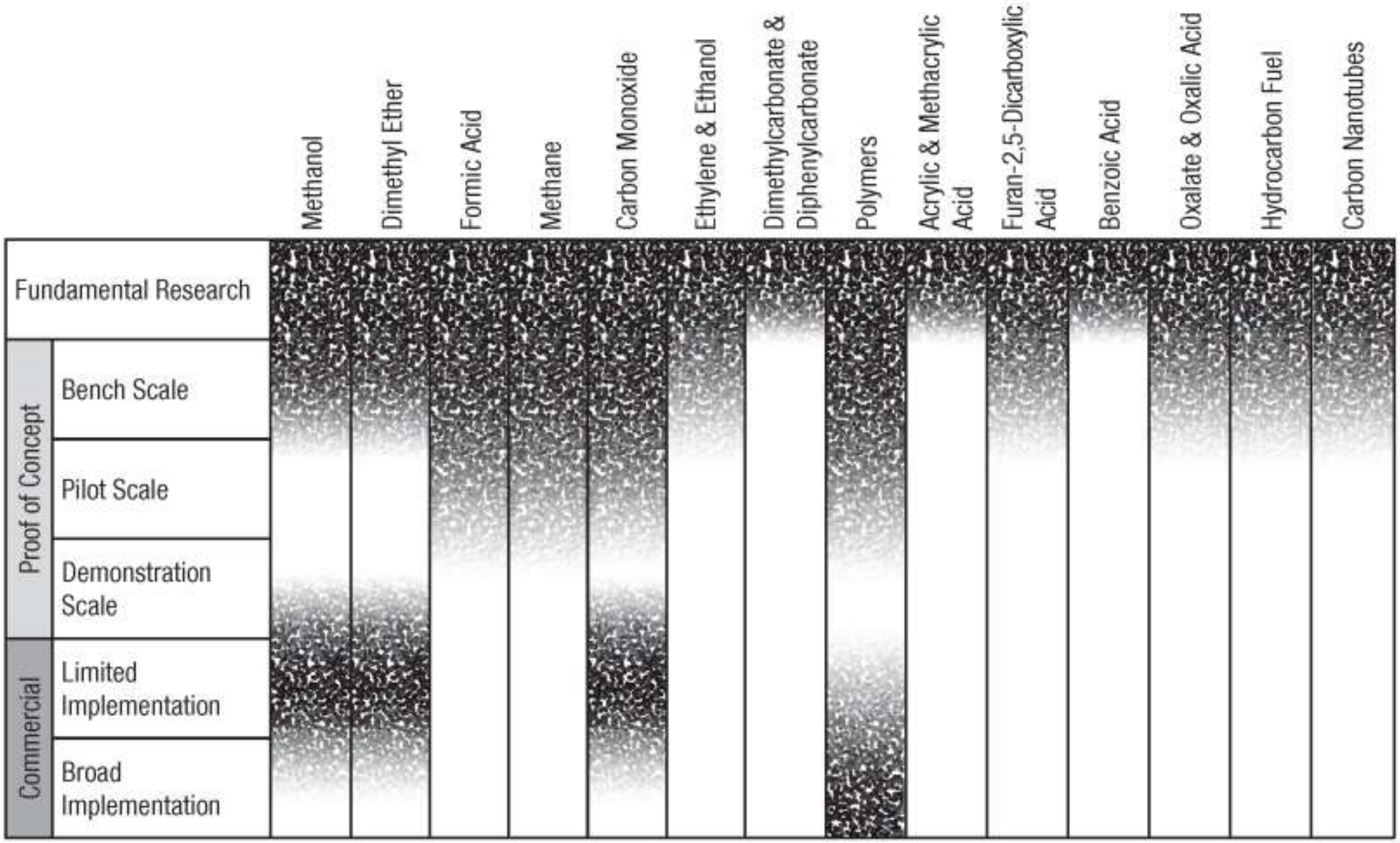
Annex Slides

Mineral Carbonation Research Agenda

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 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 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 Utilization



Chemical Utilization – Key Barriers

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

Chemical Utilization Research Agenda

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 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 dioxide conversion processes that are relevant at commercial scale.
Pathways to new products	Research is needed to develop processes that produce non-traditional 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.

Tools – 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, 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 clean up, 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 towards 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.

Finding: 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.

Tools – 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.
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 is needed to establish codes for use.