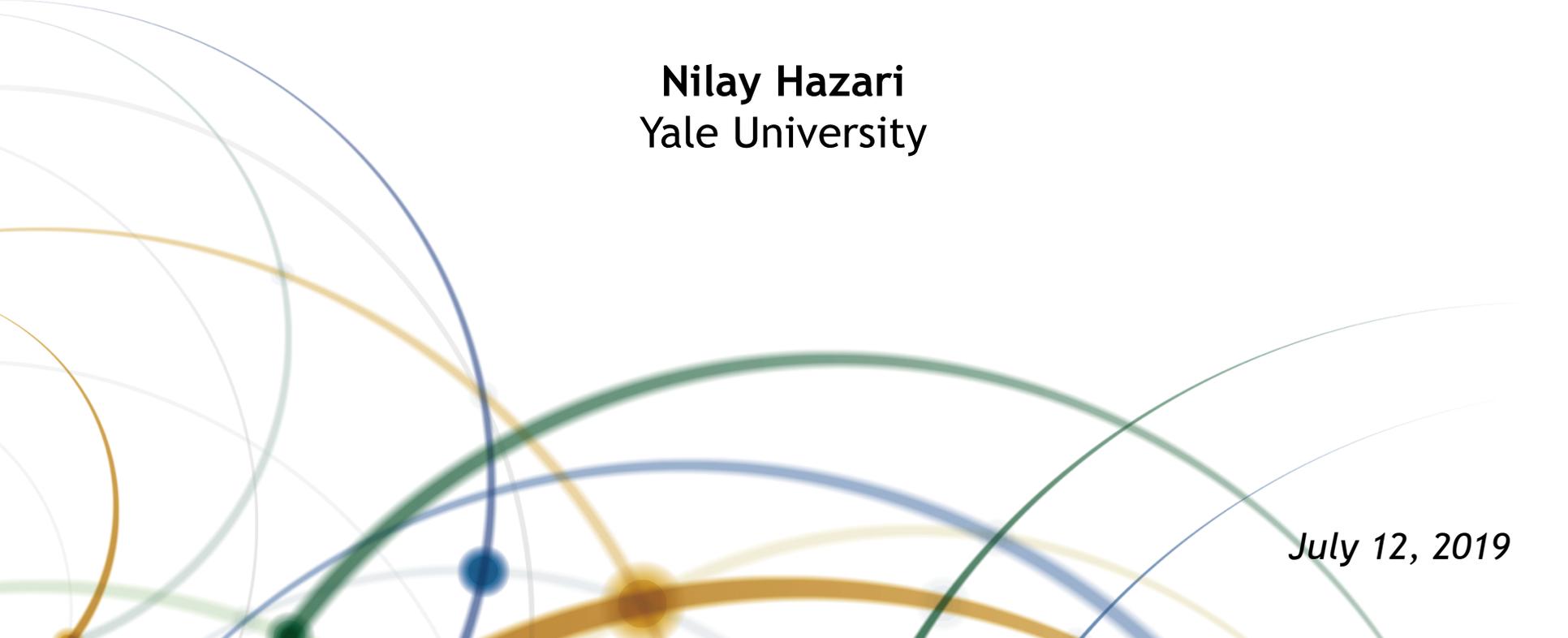


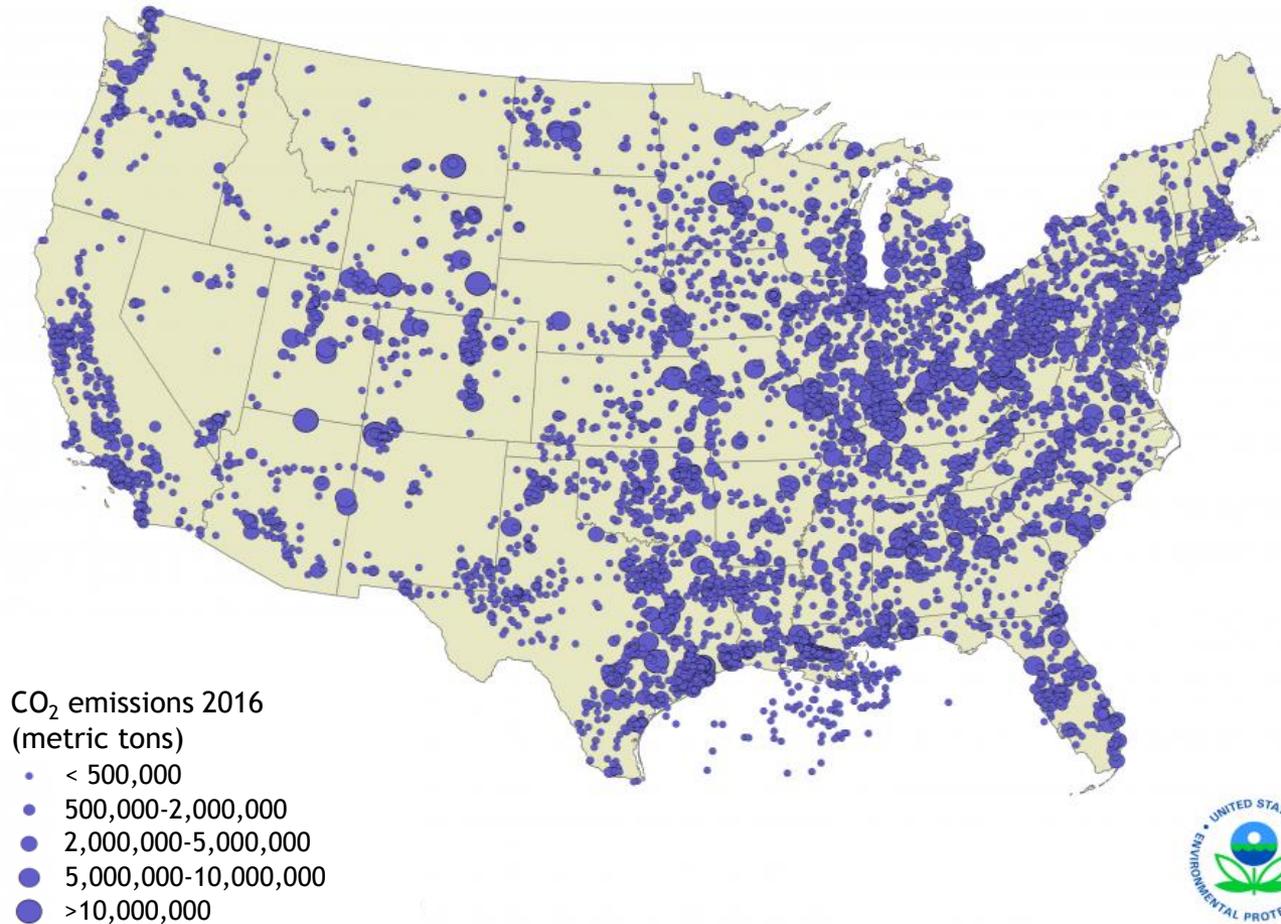
Gaseous Carbon Waste Streams Utilization: Status and Research Needs

Nilay Hazari
Yale University

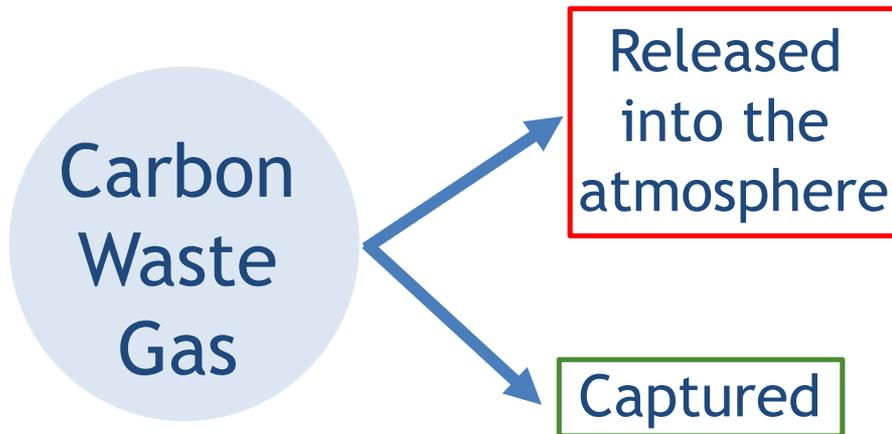
July 12, 2019



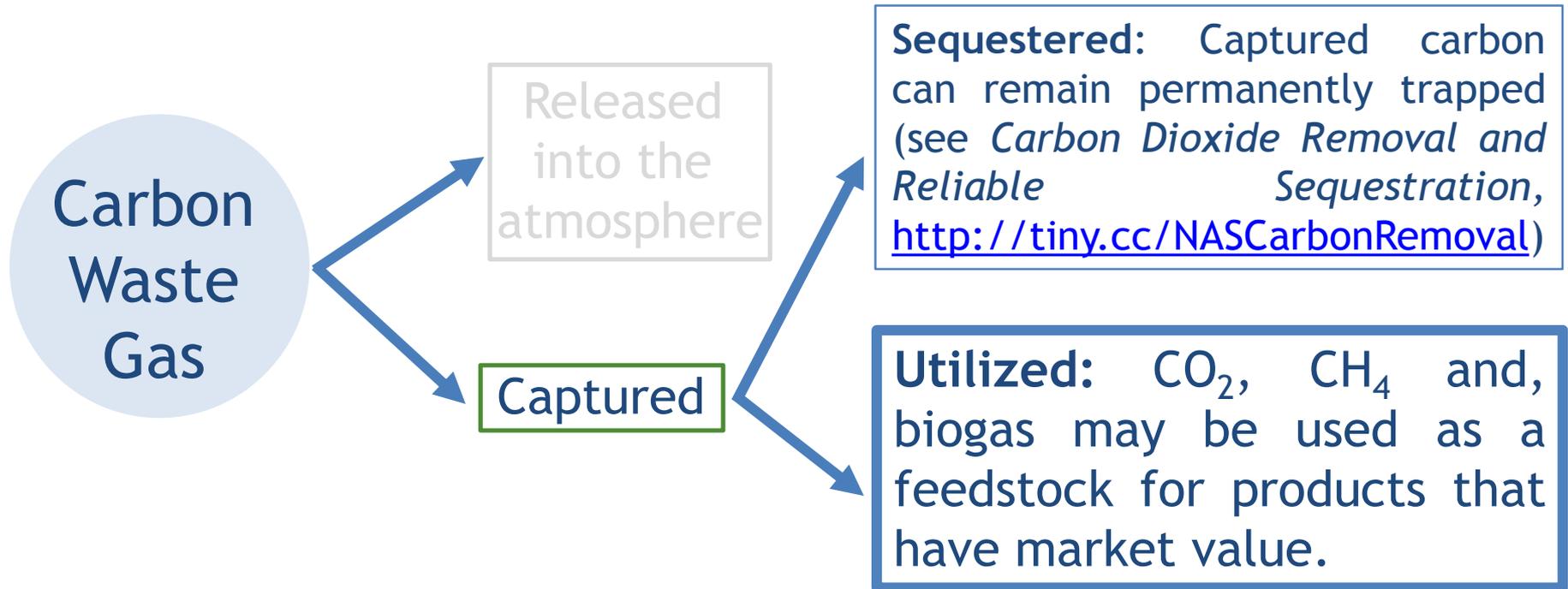
The study was motivated by an interest in increasing carbon waste gas utilization.



Carbon waste gas utilization is part of a capture, utilization, and sequestration system.



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Scale of products made from utilization is small relative to the scale of carbon emissions.

The report addresses the study Statement of Task.

1. **Assess the global status and progress of carbon utilization technologies** in practice today that utilize waste carbon (including carbon dioxide, methane, and biogas).
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.

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Study Committee



David Allen, NAE (Chair), University of Texas, Austin



Mark Barteau, NAE, Texas A&M University



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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.

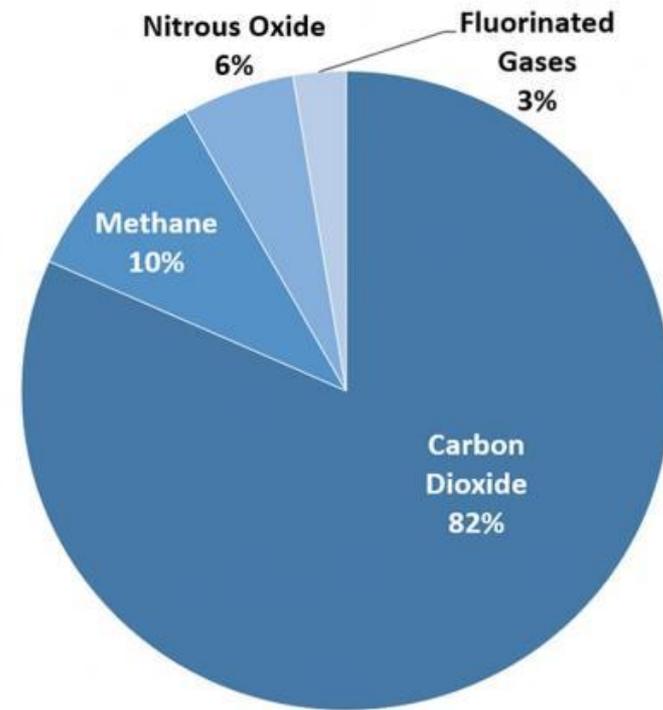
The committee gathered data from a variety of public sources over 11 months.

- Committee knowledge and experience
- Data gathering conducted at 3 committee meetings and 2 webinars
- Peer-reviewed research literature
- Community input through study website

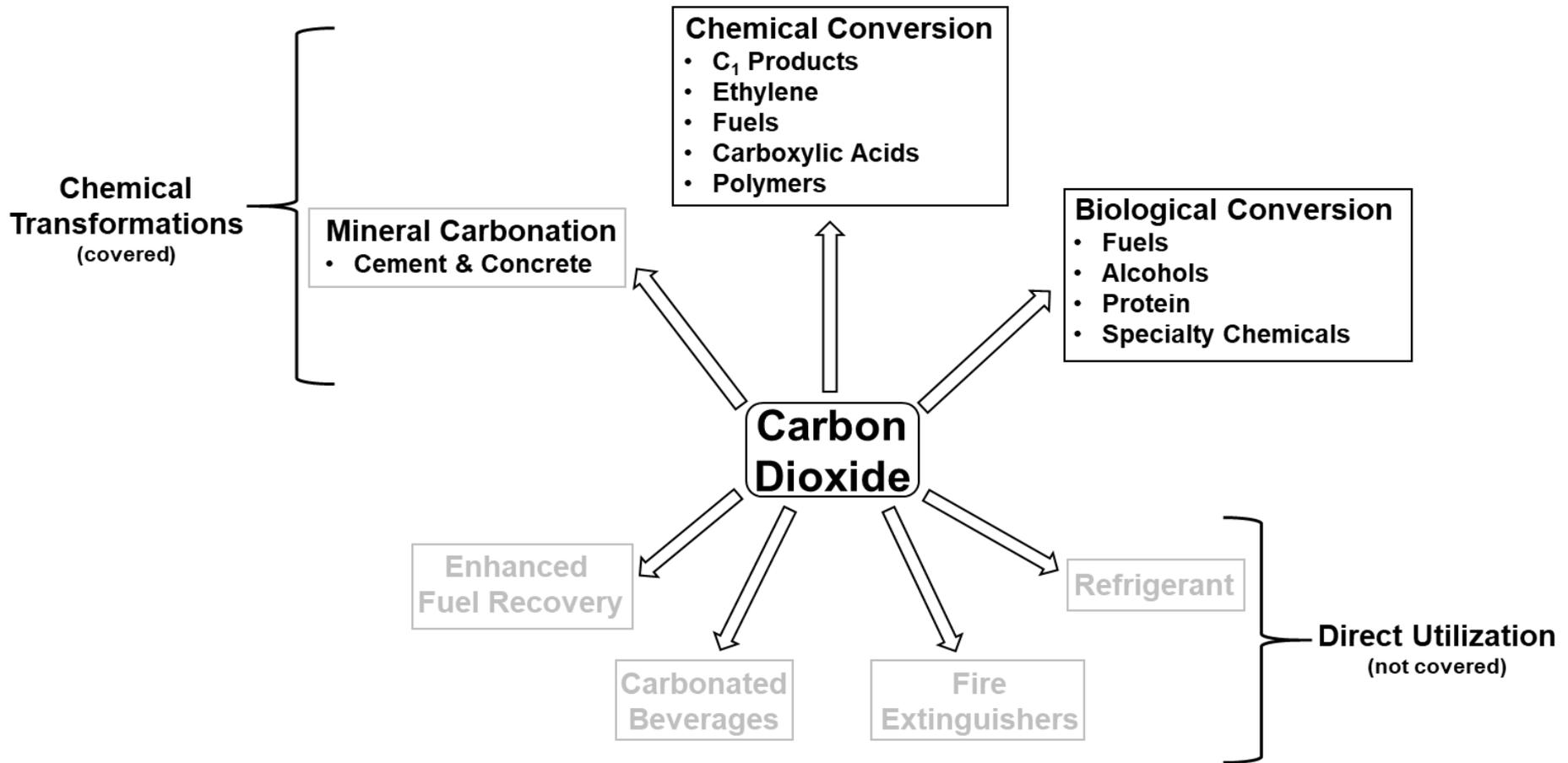
The committee considered research needs for CO₂ and methane waste gas utilization.

CO₂ was the focus because it is more abundant than methane and has greater opportunity for utilization at large scale.

Overview of Greenhouse Gas Emissions in 2017



Report focused on utilization pathways that result in chemical transformation of CO₂ into a valuable product.



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

- **Enabling technology and resources** that are key to realizing carbon utilization with net reduction in greenhouse gases.
- **Life-cycle assessment and techno-economic analysis** are important evaluation tools for carbon utilization technologies.
- Carbon dioxide waste gas utilization follows **three technical pathways**.
 - Mineralization, chemical, and biological utilization

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Examples of enabling technology and resources.

- Issues associated with the waste gas:
 - Separation, purification, transport, and delivery.



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- Reducing emissions associated with co-reagents:
 - Hydrogen
 - Electricity
 - Heat



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Basic scientific advances are required in these areas as well as in waste gas utilization.

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Life-cycle assessment (LCA) and technoeconomic analysis (TEA)

- LCA evaluates the total energy requirements and environmental impacts.
- Improvements needed in:
 - Benchmarking to standardize results.
 - More early stage LCA assessments.
 - Tools for assessing disruptive change.

Life-cycle assessment (LCA) and technoeconomic analysis (TEA)

- LCA evaluates the total energy requirements and environmental impacts.
- Improvements needed in:
 - Benchmarking to standardize results.
 - More early stage LCA assessments.
 - Tools for assessing disruptive change.
- TEA evaluates the technical and economic viability of a new technology.
- Improvements needed in:
 - Standardized and transparent inputs.
 - More early stage TEA assessments.
 - More understanding of societal acceptance of waste gas products.

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

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Economic Factors

Economic value

Scale, market capacity,
and market penetration

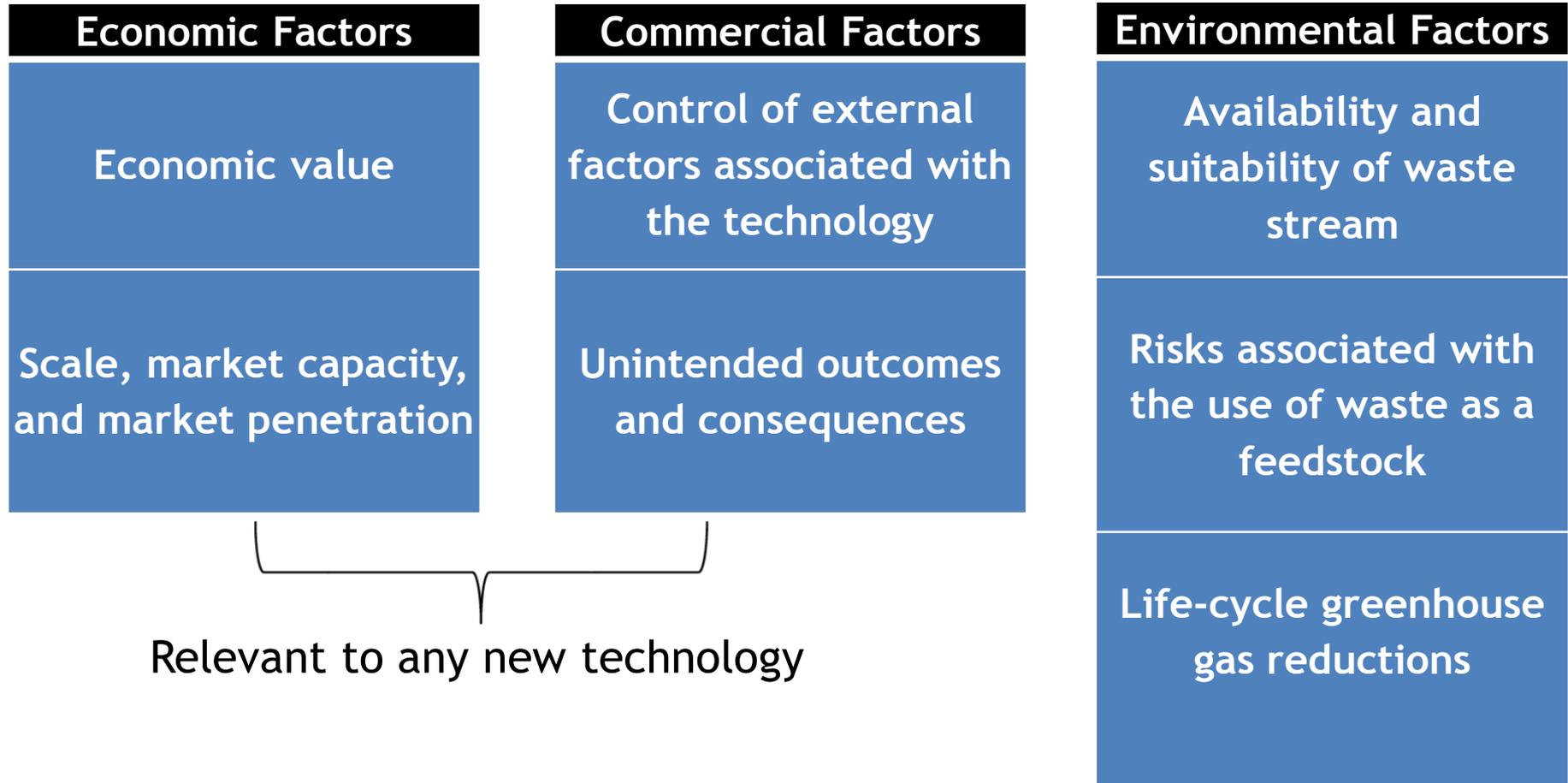
Each factor has one or more
criteria associated with it

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

Economic Factors	Commercial Factors
Economic value	Control of external factors associated with the technology
Scale, market capacity, and market penetration	Unintended outcomes and consequences

Each factor has one or more criteria associated with it

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



The committee did not apply the criteria to assess different technologies.

- 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 organized the report around key features of the carbon utilization system.

- Enabling technology and resources that are key to realizing carbon utilization with net reduction in greenhouse gases.
- Life-cycle assessment and techno-economic analysis are important evaluation tools for carbon utilization technologies.
- Carbon dioxide waste gas utilization follows **three technical pathways**.
 - Mineralization, chemical, and biological utilization

Mineral Carbonation Processes

- Transform carbon dioxide into mineral carbonates, which can be used to make concrete and cements.
- Due to the scale of cement production and lifetime of the products mineral carbonation represents a significant opportunity.



50 billions tons of
construction materials
generated per year

Mineral Carbonation Processes

- Transform carbon dioxide into mineral carbonates, which can be used to make concrete and cements.
- Due to the scale of cement production and lifetime of the products mineral carbonation represents a significant opportunity.
- Research is required to improve many areas of mineral carbonation including:
 - Understanding the fundamental chemical factors that **control the relative rates of carbonation and hydration**.
 - Integrating mineralization processes with existing carbon capture technologies.
 - **Developing physical and instrumental methods**, improved modeling, and performance-based criteria for assessing product properties.
 - Developing of **new analytical tools** for studying carbonation reactions.

Biological Utilization Processes

- Use microorganisms to convert carbon dioxide into materials such as fuels, polymers, and fine and commodity chemicals.

Platform	Product	Stage of Development				
		Proof of Concept			Commercial	
		Bench Scale	Pilot Scale	Demonstration Scale	Limited Implementation	Broad Implementation
Green Algae	<i>Fuels</i> : Biodiesel	█	█	█	█	█
	<i>Fuels</i> : Renewable diesel/gasoline			█	█	
	<i>Protein</i> : Animal feed or human food			█	█	
	<i>PUFAs</i> : Eicosapentaenoic acid	█		█	█	█
	<i>PUFAs</i> : Docosahexaenoic acid	█		█	█	
	<i>Pigments</i> : Astaxanthin	█		█	█	█
Cyanobacteria	<i>Fuels</i> : Ethanol, butanol, etc.	█				
	<i>Chemicals</i> : isoprene, ethylene, etc.	█				
Chemolithotrophs	Acetogens (feedstock: CO ₂)	█				
	Two-stage process (feedstock: syngas CO ₂ and CO or H ₂)	█				
	Acetogens (feedstock: CO)	█				█
Bioelectrochemical systems	Succinate	█				
	Acetate	█				
	Alcohols	█				
	Pyruvate	█				

Key barriers for each product identified

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.

Chemical Utilization Processes

- Use chemical methods including thermal, electrochemical, and photochemical processes to convert carbon dioxide into materials such as fuels, polymers, and fine and commodity chemicals.
- Some processes are already operating commercially, but these are typically only scalable in certain geographic locations.



Chemical Utilization Processes

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Product	Stage of Development				
	<i>Proof of Concept</i>			<i>Commercial</i>	
	Bench Scale	Pilot Scale	Demonstration Scale	Limited Implementation	Broad Implementation
Carbon Monoxide	██████████	██████████		██████████	
Dimethyl Ether	██████████	██████████		██████████	
Formic Acid	██████████	██████████	██████████		
Methanol	██████████	██████████		██████████	
Methane	██████████	██████████		██████████	
Ethylene and Ethanol	██████████				
Dimethylcarbonate	██████████				
Hydrocarbon Fuels	██████████	██████████			
Acrylic and Methacrylic Acid	██████████				
Furan-2,5-Dicarboxylic Acid	██████████				
Benzoic Acid	██████████				
Oxalate and Oxalic Acid	██████████	██████████		██████████	
Polymers	██████████	██████████	██████████	██████████	██████████
Carbon Nanotubes	██████████				

Chemical Utilization Processes - Barriers

Product	Key Barriers
Methanol	<ul style="list-style-type: none"> • Direct hydrogenation of CO₂: low conversion per pass, catalyst inhibition by water • Electroreduction of CO₂ in water: high overpotentials, low selectivity
Dimethyl Ether	<ul style="list-style-type: none"> • Similar challenges to methanol production
Formic Acid	<ul style="list-style-type: none"> • Homogeneous hydrogenation of CO₂: stoichiometric added base required for high turnover, separation of formic acid from reaction medium/base recycling • Photoelectrochemical and electrochemical reduction of CO₂: poor catalyst stability, separation of formic acid from reaction medium
Methane	<ul style="list-style-type: none"> • Electroreduction of CO₂: very high overpotentials, low selectivity
Carbon Monoxide	<ul style="list-style-type: none"> • Electroreduction of CO₂: High flux of CO₂R to cathode required, low per-pass conversion
Ethylene and Ethanol	<ul style="list-style-type: none"> • Electroreduction of CO₂: low selectivity, poor catalyst stability
Dimethylcarbonate and Diphenylcarbonate	<ul style="list-style-type: none"> • Alcohol/CO₂ condensation: low per-pass conversion • Alcohol/urea condensation: low selectivity, low per-pass conversion
Polymers	<ul style="list-style-type: none"> • Polycarbonates: tendency of product to decompose into cyclic carbonates; high-purity CO₂ required • Polyether carbonates: understanding catalyst structure-polymer property relationship for tailored products
Acrylic and Methacrylic Acid	<ul style="list-style-type: none"> • Very low catalyst turnover frequencies; requirement for stoichiometric additives
Furan-2,5-Dicarboxylic Acid	<ul style="list-style-type: none"> • Low reaction rates, salt recycling process for carbonate regeneration not proven
Benzoic Acid	<ul style="list-style-type: none"> • Requirement for stoichiometric additives
Oxalate and Oxalic Acid	<ul style="list-style-type: none"> • High overpotential, low selectivity
Hydrocarbon Fuel	<ul style="list-style-type: none"> • Low selectivity, lack of understanding of carbon-carbon bond formation steps
Carbon Nanotubes	<ul style="list-style-type: none"> • Properties of currently produced carbon fibers not suitable to act as replacements for carbon fibers

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Chemical Utilization - General Barriers

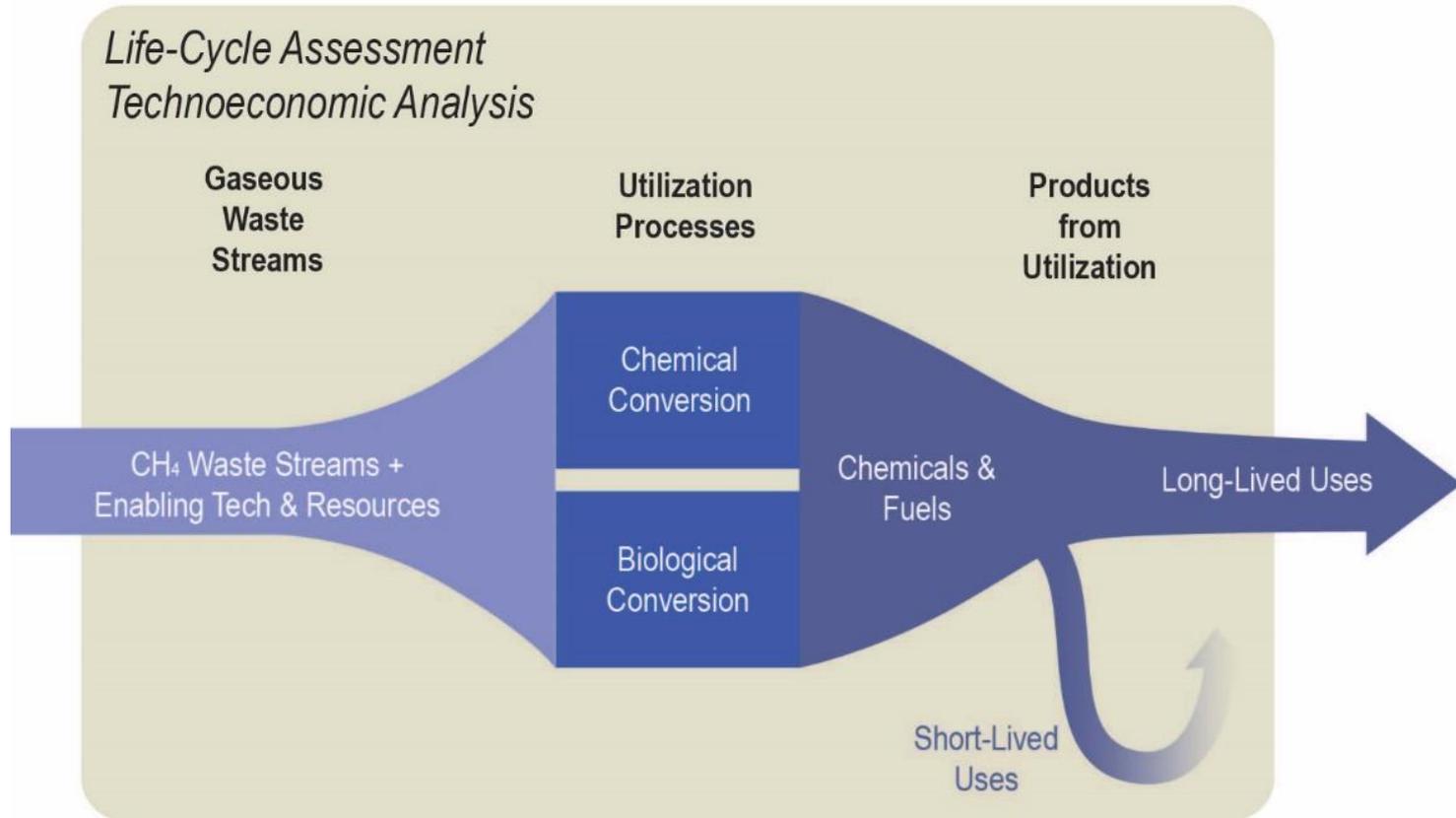
- Improved catalyst design and development including:
 - Catalysts that can form C-C bonds.
 - Catalysts that can form non-traditional products.
 - Catalysts that are compatible with strategies for carbon dioxide capture.
 - Catalysts that can operate with low purity carbon dioxide.
 - Catalysts that have increased stability.
- Development of systems that do not require stoichiometric additives.
- Integration of reactor design with catalyst technology.
- Problems associated with electrochemical systems:
 - Low per pass conversions.
 - Reaction of carbon dioxide with the electrolyte.
 - Catalysts that are compatible with strategies for carbon dioxide capture.

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.

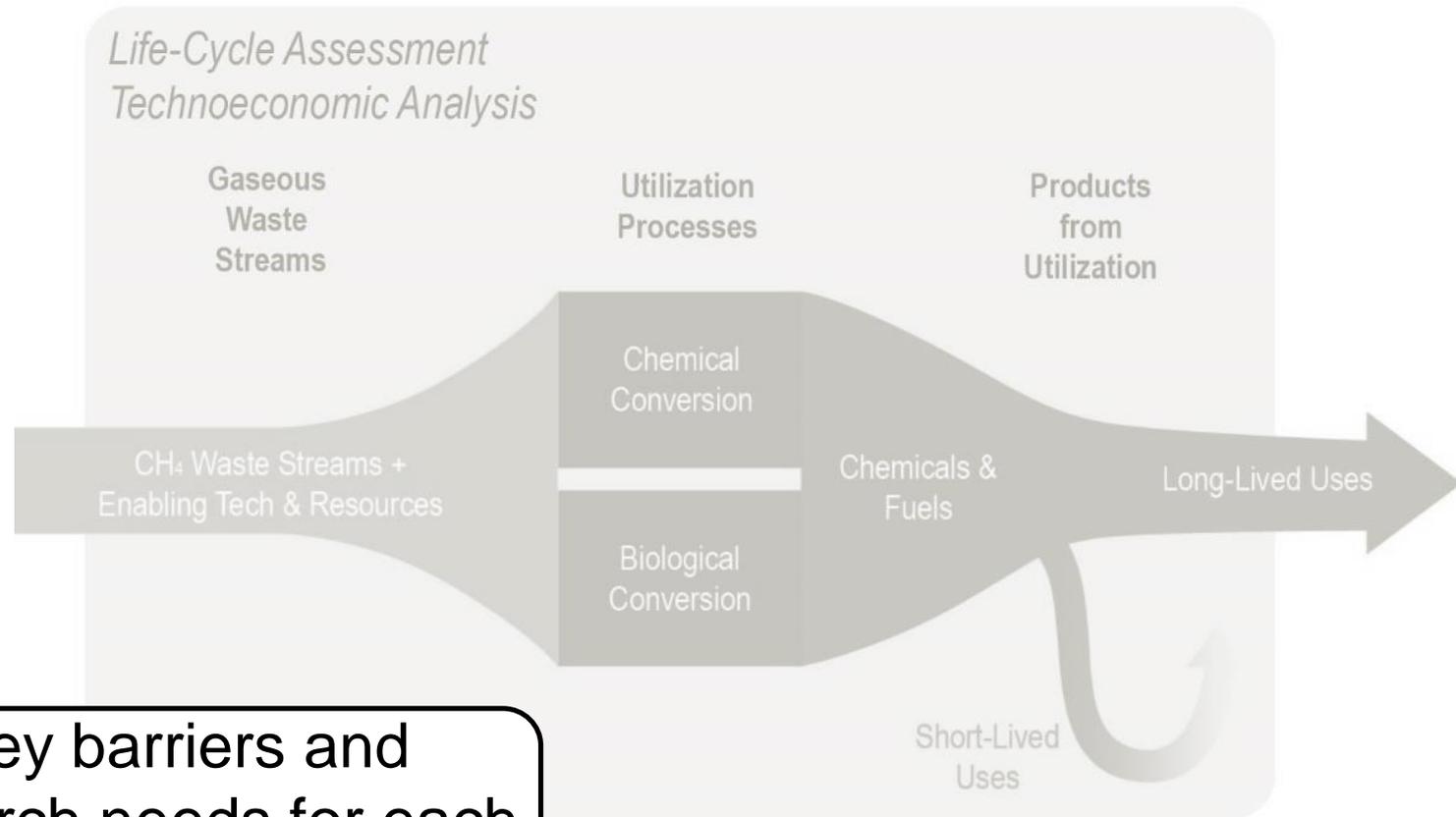
Methane and Biogas Utilization

CH₄ Waste Gas Valorization



Methane and Biogas Utilization

CH₄ Waste Gas Valorization



Key barriers and research needs for each product identified

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.

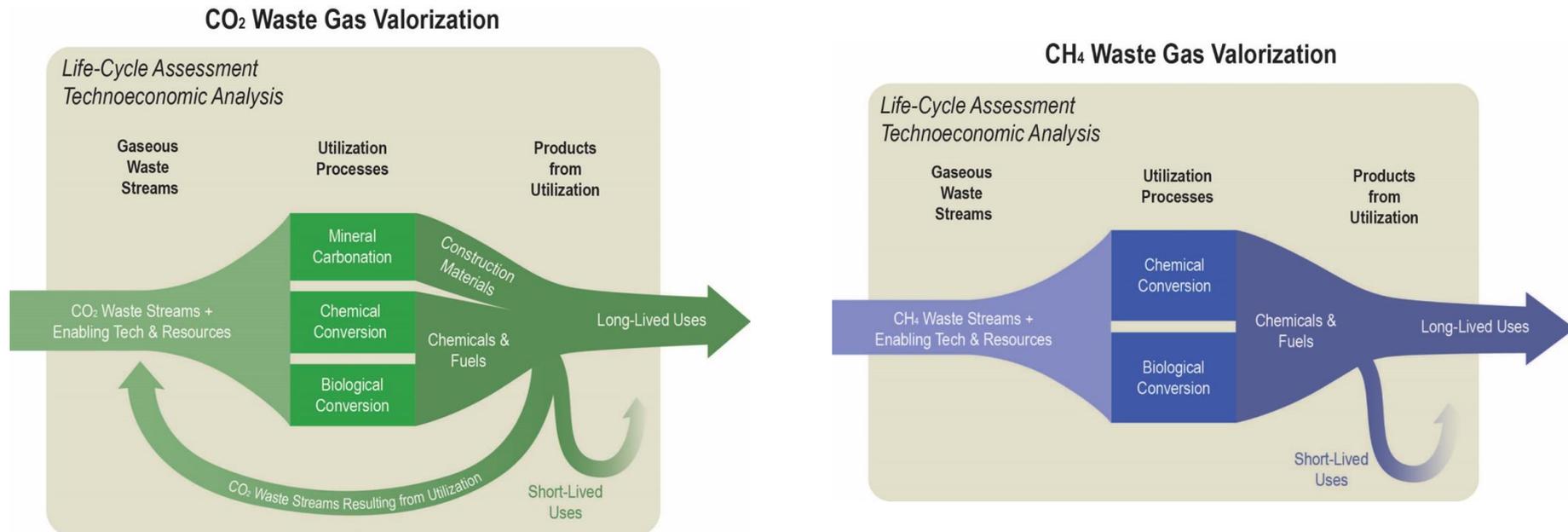
Specifically:

- 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.



Carbon utilization should be one facet of our long-term strategy to reduce carbon emissions.

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