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PNNL-35588

Emerging Technologies Review: Carbon Capture and Conversion to Methane and Methanol

January 2024

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Prepared for the Air Force Civil Engineer Center
under a Work-For-Others Agreement with the U.S. Department of Energy

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Richland, Washington 99354

Executive Summary

A majority of missions in the Department of the Air Force (DAF) depend on both energy and water. The 2021 Air Force Installation Energy Strategic Plan embraces this dependency and outlines a path to greater mission assurance through the realization of more resilient energy and water systems. The previous energy strategic plan placed equal weight on resilience, cost-effectiveness, and cleaner energy technologies. The new plan emphasizes a focus on resilience and mission-centric efforts.[1] The 2022 Air Force Climate Action Plan[2] aligns with the Energy Strategic Plan in its third priority, where it calls on the DAF to optimize energy use and pursue alternative energy sources. The Air Force Civil Engineer Center has tasked Pacific Northwest National Laboratory with investigating emerging technologies to inform the Air Force's understanding of the technology and to guide key considerations for implementing technologies that are resilient and alternative sources to the traditional methods used in the Air Force today.

In response to these DAF needs, this report describes the emerging technology to capture carbon as a waste product and convert this to methane and methanol for deployment as a fuel on Air Force installations. In addition to reducing CO_2 in the atmosphere and as a result helping to alleviate climate change, an Air Force installation with a carbon capture and conversion plant can produce its own fuel without depending on external fuel supply lines, which are vulnerable to disruption and attack.

As shown in Figure ES.1, a typical process for carbon capture and conversion to synthetic fuel consists of the following:

1. **CO_2 point source**, where fossil fuel is burned in a power plant or other manufacturing/maintenance facilities to generate flue gas (mainly N_2, O_2, H_2O, and CO_2)
2. **CO_2 capture unit** to separate CO_2 in the flue gas from other gas components and release clean flue gas (CO_2 lean) to the environment
3. **CO_2 compression and transportation** (optional) to deliver captured CO_2 from the CO_2 capture unit to a CO_2 conversion unit at a desired pressure; the transportation step is not needed if CO_2 capture and conversion units are co-located
4. **CO_2 conversion unit** to react the captured CO_2 with H_2 at elevated temperature and pressure to form synthetic fuels (i.e., methane or methanol) that can be used in the existing Air Force facilities ("Product Consumers" in the figure) originally consuming fossil fuels.
5. **H_2 supply** for conversion**.** This technology can achieve peak decarbonization by utilizing green H_2 made through water electrolysis with renewable energy, despite the higher raw material expense.

[1] *Air Force Installation Energy Strategic Plan*, https://www.af.mil/Portals/1/documents/2021SAF/01_Jan/AF_Installation_Energy_Strategic_Plan_15JAN2021.pdf

[2] *Air Force Climate Action Plan*, https://www.safie.hq.af.mil/Programs/Climate/

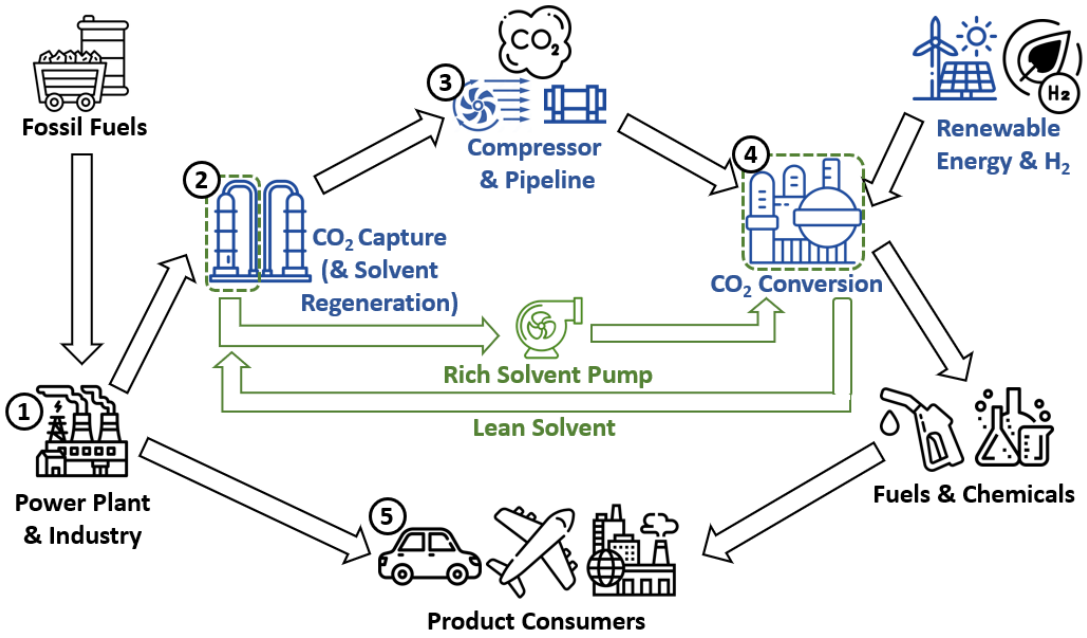

Figure ES.1. Carbon Capture and Conversion Main Components

Note that an alternative configuration (colored green in Figure ES.1) integrates the capture and conversion process, which may offer higher efficiency and cost less than the conventional configuration described above. In general, the carbon capture and conversion technology has the potential to reduce harmful greenhouse gas emissions from fossil fuel plants and convert these into usable alternative energy resources, modernize the existing energy infrastructure without major modifications for using zero-carbon-based energy sources, and break down barriers in the transition to clean energy by enabling the direct use of renewable sources (i.e., renewable H_2 and electricity).

There are a number of potential products that can be made with captured CO_2, including methane as an energy resource, methanol as an energy resource or for chemical production, sustainable aviation fuel (from methanol), and e-fuels (methane or methanol as energy carriers for renewables). These CO_2-derived alternative energy sources can play a surprisingly diverse role in powering and supporting the operations of an Air Force installation. Below are some key use cases:

- Power generation (i.e., cogeneration plants, backup power), heating and hot water (i.e., building heating, domestic hot water)
- Fueling vehicles and equipment (i.e., ground support equipment, fleet vehicles)
- Training and maintenance (i.e., jet engine testing for alternative fuel, metalworking, and welding).

Carbon capture and conversion technology has the following key characteristics that could make it a compelling technology for the Air Force or military installations to optimize energy use and pursue alternative energy sources:

- **Resilient**: Capturing and converting CO_2 to synthesis fuels slows down climate change, boosts resiliency by taming extreme weather events, and strengthens energy security by diversifying sources.

- **Cleaner**: The technology captures CO_2 from clean existing Air Force facilities and produces low-carbon fuels as alternatives to fossil fuels, which can revolutionize the energy landscape of existing facilities with closed-loop carbon utilization.
- **Cost-effective with Policy Support**: The cost of carbon capture and conversion is steadily declining due to government and privately funded scale-up projects and federal/state incentives.

There are many factors to consider when implementing a carbon capture and conversion process. Key factors are listed below.

- **Technical consideration**: A rich diversity of carbon capture and conversion technologies is in development, offering a range of advantages and disadvantages depending on their technology readiness levels. Notably, for each critical component in the process, there is at least one mature technology ready for potential implementation at Air Force facilities. Alternative technologies hold immense promise for future efficiency improvement and cost reductions, but require pilot-scale testing before full-scale installation at Air Force facilities.
- **Regulatory and permitting**: Regulatory approval and permitting will be required for implementing carbon capture and conversion technology.
- **Potential risks**: A successful installation requires early and continual engagement and transparent communication with the public and stakeholders to address social concerns and a comprehensive project environmental review and permitting process to address environmental concerns. Other risks related to cost, policy, and technology should be addressed in the planning stage.
- **Economic consideration**: Advancing the technology maturity of emerging technologies and access to policy supports and incentives are critical to project success.
- **Operational consideration**: Flexible operation capacity is required to manage changes to supply and demand. Robust maintenance plans should be developed for all equipment and critical materials used in the process (solvent, sorbent, catalyst, etc.).
- **Siting consideration**: The ideal location will have an onsite CO_2 source and readily available water for renewable hydrogen generation, and access to necessary utilities.

To advance the implementation of carbon capture and conversion at Air Force sites, it is recommended that the Air Force start with a pilot plant to test the feasibility, demonstrate basic functions and performance, and ensure operational resilience of the technology before any full-scale installation. Implementing a pilot plant would necessitate a number of steps, including site selection, technology screening, feasibility assessment, financial planning, regulatory compliance, engineering design, construction, monitoring, and continuous improvement. Starting with a pilot plant would offer valuable information for the subsequent phases of the project, which should assist with decision-making, resource allocation, and the overall success of the carbon capture initiative. It is important to emphasize that during the technology selection steps, the Air Force should pay close attention to the status of ongoing U.S. Department of Energy projects aiming to advance and de-risk low-cost emerging technologies. To select a technology and decide when and where to deploy a carbon capture and conversion plant, the DAF should consider all operational, technical, regulatory, environmental, and economic factors.

Acronyms and Abbreviations

AFCEC	Air Force Civil Engineer Center
CAA	Clean Air Act
CCS	carbon capture and sequestration
CRI	Carbon Recycling International
DAF	Department of the Air Force
DOE	U.S. Department of Energy
EEMPA	N-(2-ethoxyethyl)-3-morpholinopropan-1-amine
EPA	U.S. Environmental Protection Agency
FAST	Fixing America's Surface Transportation
GHG	greenhouse gas
HAP	hazardous air pollutant
IGCC	integrated coal gasification combined cycle
LCFS	Low Carbon Fuel Standard
MTBE	methyl tert-butyl ether
MEA	monoethanolamine
Mtpa	metric tons per annual
NAAQS	national ambient air quality standard
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NETL	National Energy Technology Laboratory
NPDES	National Pollutant Discharge Elimination System
NSPS	New Source Performance Standards
NSR	New Source Review
PNNL	Pacific Northwest National Laboratory
R&D	research and development
RNG	renewable natural gas
SAF	sustainable aviation fuel
SIC	Standard Industrial Classification
SNG	synthetic natural gas
TEA	techno-economic analysis
TREMP	Topsøe Recycle Energy-Efficient Methanation Process
TRL	technology readiness level
V/L	vapor-liquid
V/S	vapor-solid

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1.0 Introduction

A majority of missions in the Department of the Air Force (DAF) depend on both energy and water. The 2021 Air Force Installation Energy Strategic Plan embraces this dependency and outlines a path to greater mission assurance through the realization of more resilient energy and water systems. The previous energy strategic plan placed equal weight on resilience, cost-effectiveness, and cleaner energy technologies. The new plan emphasizes a focus on resilience and mission-centric efforts: “Resilience has become central to DAF efforts” (Air Force 2021). The 2022 Air Force Climate Action Plan (Air Force 2022) aligns with the Energy Strategic Plan in its third priority, where it calls on the DAF to optimize energy use and pursue alternative energy sources.

Within this new resilience focus, the Air Force Civil Engineer Center (AFCEC) has tasked Pacific Northwest National Laboratory (PNNL) with investigating emerging technologies to inform the Air Force’s understanding of the technology and to guide key considerations for implementing technologies that are resilient and alternative sources for energy compared to the traditional methods used in the Air Force today.

In response to these DAF needs, this report describes the emerging technology to capture carbon as a waste product and convert this to methane and methanol for deployment as a fuel to be used at existing Air Force facilities. As described in this report, carbon capture and conversion to synthetic fuels (i.e., methane and methanol) is a chemical process that produces zero-carbon or even negative-carbon fuels from carbon dioxide (CO_2).

This carbon capture technology provides alternative energy sources that can be directly used in existing Air Force infrastructure (i.e., transportation, power generation, manufacturing, maintenance, etc.) with minimum retrofitting, and it provides a pathway for the DAF to move toward carbon pollution-free energy sources. In addition, the carbon capture and conversion process offers low-cost grid-balancing solutions for low-carbon energy [i.e., green hydrogen (H_2) and renewable electricity] penetration by solving associated energy transportation and storage challenges. It is a critical element in the U.S. and global efforts to achieve net-zero emissions by 2050.

Section 2.0 of this report provides a technical overview of the technology, with more in-depth technical details in Appendix A. Section 3.0 outlines the technical considerations, including technical maturation, for DAF to consider in its selection choices. Related to ensuring this technology can meet DAF’s needs, Section 4.0 describes regulatory considerations; Section 5.0 outlines potential risks; Section 6.0 reviews economic considerations; Section 7.0 outlines operational considerations such as supply/demand, change management, and maintenance requirements; Section 8.0 reviews implementation and siting considerations; and Section 9.0 provides recommendations and a path forward based on all the data from the previous sections. Appendix A provides additional technical detail to support DAF in making an informed decision.

2.0 Technology Description

Carbon capture and conversion to synthetic fuels (i.e., methane and methanol) is a chemical process that produces zero-carbon or even negative-carbon fuels from CO_2. This technology provides alternative energy sources that can be directly used in existing DAF infrastructure (i.e., transportation, power generation, manufacturing, maintenance, etc.) with minimum retrofitting, and it provides a pathway for DAF to move toward carbon-pollution-free energy sources. In addition, carbon capture and conversion offers low-cost grid-balancing solutions for low-carbon energy [i.e., green hydrogen (H_2) and renewable electricity] penetration by solving associated energy transportation and storage challenges. It is a critical element in the U.S. and global efforts to achieve net-zero emissions by 2050.

Several CO_2 capture and conversion technologies have been developed over the past few decades. Presently, a number of mature technologies are readily available for Air Force implementation, although these require significant upfront investment and have high energy consumption. Breakthrough technologies with potential to significantly reduce the costs are under development, for which bench/pilot-scale testing has been successful. Large-scale demonstration is on the way, of which some examples are provided in Section 3.2. This section describes the beneficial characteristics, the process and key components in the entire supply chain of methane and methanol production via CO_2 capture, and conversion and configuration options.

2.1 Beneficial Characteristics

While Section 2.2 describes the process of carbon capture and conversion, this short overview provides its overall benefits, including the following:

- Reduce harmful greenhouse gas (GHG) emissions from fossil fuel plants and convert these into usable alternative energy resources.
- Modernize existing energy infrastructure without major modifications for using zero-carbon-based energy sources.
- Break down barriers to the transition to clean energy (i.e., renewable H_2 and electricity) by enabling the direct use of renewable sources.

Carbon capture and conversion has the following key characteristics that could make it a compelling technology for Air Force or other military installations.

- **Resilient**: Carbon capture and conversion directly prevents the emission of CO_2 into the atmosphere, slowing climate change, which helps to build resilience by reducing the intensity of extreme weather events. It also reduces reliance on fossil fuels, enhances energy security, and increases the resilience of energy systems to disruptions by diversifying energy sources.
- **Cleaner**: By capturing CO_2, this technology removes a potent GHG from the atmosphere, directly decarbonizing the existing facilities. By converting CO_2 to methane or methanol, the technology creates a clean energy source that can replace fossil fuels. This technology revolutionizes the energy landscape of existing facilities built on fossil energy by creating a closed-loop carbon utilization system to adopt rapid energy transition to renewables.

- **Cost-effective Efforts**: Numerous projects have been conducted to advance and scale-up the technologies, which can significantly reduce the operation cost and capital investment of carbon capture and conversion. Meanwhile, several federal-level incentives and policies supporting carbon capture and low-carbon fuel production are available in the United States to accelerate successful business cases.

2.2 Components and Process

The process of carbon capture and conversion to synthetic fuel consists of CO_2 point source, CO_2 capture, CO_2 compression and transportation (optional), CO_2 conversion, and supply of renewable H_2. As shown in Figure 2.1, flue gas (mainly N_2, O_2, H_2O, and CO_2) from the power generator or other manufacturing/maintenance facilities burning fossil fuels (item 1) is fed to a carbon capture unit (item 2) to separate CO_2 from other gas components. From the capture unit, clean flue gas (CO_2 lean) is discharged to the environment, and high-purity CO_2 is compressed and transported via pipeline (item 3) to a CO_2 conversion unit (item 4). In the CO_2 conversion unit, CO_2 is reacted with H_2 to form synthetic fuels (methane or methanol). The synthetic methane can be used as an alternative energy source in the existing Air Force facilities (item 5) that use natural gas, without any retrofitting. The synthetic methanol can be used as a fuel blend in various vehicles or as a feedstock to produce sustainable aviation fuel that would need to be approved by associated standards from the American Society of Testing and Materials.

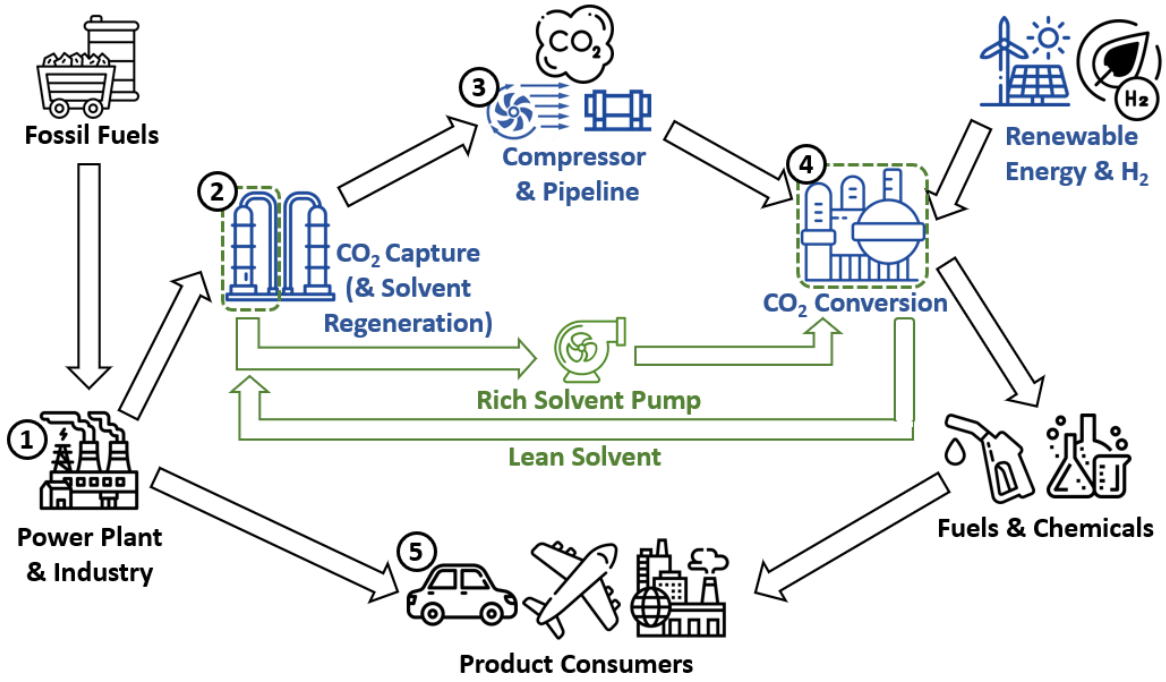

Figure 2.1. Key Components and Configuration of Carbon Capture and Conversion

2.2.1 CO_2 Point Sources

Carbon capture starts with identifying CO_2 sources. Electricity and industry are the top two source sectors internationally and in the United States (EPA 2021). Fossil fuels are combusted and released in a flue gas that contains concentrated CO_2 (typically a CO_2 concentration of 4-12%). The flue gas is traditionally released into the atmosphere and accelerates global

warming. Capturing CO_2 from flue gas is easier than capturing it directly from the air because flue gas has a higher CO_2 concentration.

There are three approaches for integrating CO_2 capture with conversional power, fuel, and chemical production processes: pre-combustion, post-combustion, and oxy-combustion. Among these strategies, post-combustion, as shown in Figure 2.2, is the simplest strategy that can be applied to existing power generation and industrial heating facilities wherever fossil fuel is burned for energy generation. In addition, it has the most mature technologies. Therefore, post-combustion CO_2 capture is more relevant to DAF missions from the perspectives of near-term implementation, resilience, and climate control. Descriptions of other carbon capture approaches can be found in Appendix A.1, along with their advantages and disadvantages.

This report focuses on the post-combustion CO_2 capture technologies and their integration with CO_2 conversion technologies for methane and methanol production. In the post-combustion process, CO_2 is separated from flue gas (mainly N_2 and CO_2 with small amounts of O_2, H_2O, and argon) produced from a conventional fossil-fuel burning process (e.g., air-blow boiler, gas turbine, engine generator) at atmospheric pressure.

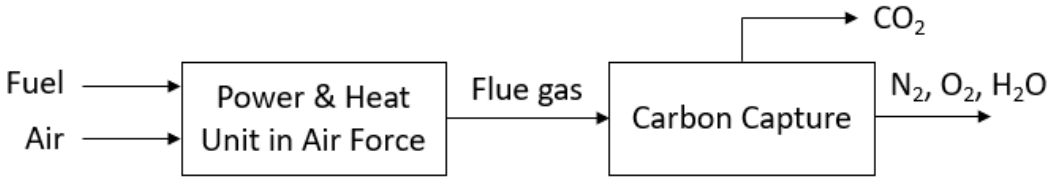

Figure 2.2. CO_2 Point Sources (post-combustion)

2.2.2 CO2 Capture Unit

In the post-combustion carbon capture unit, a relatively pure CO_2 stream (more than 95% purity) is separated from point-source flue gas. A number of technologies have been developed for post-combustion carbon capture, which fall into four general categories:

- **Absorption**: This is a two-step process using amine-based chemical solvent. In the first step, flue gas contacts with liquid solvent at near ambient conditions, where CO_2 in the gas is dissolved into the liquid solvent while other gas components stay in the gas phase. The CO_2-free flue gas is discharged to the environment. In the second step, CO_2-rich solvent is heated and then the dissolved CO_2 is released from the liquid phase back to the gas phase. This CO_2 stream has very high purity that can be used for either conversion or subsurface storage. The CO_2-lean solvent can be reused in the first step.
- **Cryogenic**: The cryogenic process operates as essentially a phase separation process at extremely low temperature. To better understand this process, imagine a giant freezer is used to capture CO_2 from flue gas and prevent it from contributing to climate change. In the process, flue gas is compressed and cooled down to around -100 to -135 °C. At this condition, CO_2 turns to solid, which is then separated from other gas components in the flue gas by filters or cyclones.
- **Membrane**: The membrane process uses a thin filter that separates CO_2 from other gases like a strainer separates food from liquid. In this process, flue gas is passed through a special membrane that is more permeable to CO_2 than other gas components. The CO_2 molecules are smaller than other gas molecules, and therefore can easily pass through the pores of the membrane, while the other gases cannot and are left behind.

- **Adsorption**: The basis of the adsorption process is similar to that of activated carbon for odor control. However, instead of using activated carbon to selectively adsorb organic compounds (odor) or air, specially designed solid sorbents with high CO_2 selectivity are used to adsorb CO_2 from flue gas, acting like the sticky surface of a fly trap to attract and hold onto CO_2 molecules while letting other gases pass through. Once the sorbent is full, the captured CO_2 is released by heating the sorbent, lowering the pressure, and/or displacing it with other gases. At this point, the sorbent can be reused.

These technologies usually consume steam and/or electricity as energy input to separate CO_2 from the flue gas. Selection of carbon capture technologies for DAF implementation could be case- or site-sensitive, highly depending on the flue gas quantity (each technology has different economies of scale), impurities in the flue gas (due to the concern of chemical tolerance of materials used in different technologies), plant footprint, access to local utilities, and access to construction materials. The variety in post-combustion carbon capture can provide DAF the flexibility to select the most suitable candidate for a given site. Table 2.1 summarizes the advantages, challenges, and representative technologies. Appendix A, Section A.2 provides detailed technology descriptions and process flow diagrams of the four technology options. Technology considerations are detailed in Section 3.0.

Table 2.1. Summary of Post-combustion CO_2 Capture Technologies

Category	Advantages	Challenges	Examples
Absorption	• Most mature technology • Many solvent types available • Great for scale-up • Great for high gas flows	• High energy penalties in general, which can be mitigated with advanced solvents • Large plant footprint • Solvent degradation	• MEA[(a)] • Shell Cansolv[(b)] • PNNL EEMPA[(a)]
Cryogenic	• High CO_2 recovery and purity (above 99%) • Great for both small and large scale • Mature for natural gas processing	• Water must be removed to prevent ice plugging • High energy penalties • Not suitable for dilute CO_2 feed	• Air Liquide Cryocap FG[(c)] • SES CCC[(d)]
Membrane	• Small plant footprint • Light weight • Low energy requirement • Suitable for low-medium gas flows	• Need more CO_2 compression • Low CO_2 purity (~95%) • Not suitable for low CO_2 concentration flue gas • Low to moderate stability through regeneration • Capital intensive for large scale	• MTR membrane[(e)]
Adsorption	• Suitable for low-medium gas flows • Compact and modular • Non-toxic materials	• Capital costs per tonne CO_2 captured become high for high flowrate	• TDA[(f)]

(a) Jiang et al. 2023. (b) James et al. 2019. (c) O'Brien et al. 2022. (d) Hoeger et al. 2021. (e) Baker et al. 2022. (f) Alptekin 2022.

Terms: MEA = monoethanolamine; EEMPA = N-(2-ethoxyethyl)-3-morpholinopropan-1-amine; MTR = Membrane Technology and Research, Inc.; FG = flue gas; CCC = Cryogenic Carbon Capture; TDA = TDA Research Inc.

Among the four carbon capture technologies described, the absorption technology using solvent is preferable because of fast reaction kinetics, enhanced mass and heat transfer, and low capture costs. It is also more convenient to handle in a continuous flow process. The following benefits make water-lean solvents superior for integrated capture and conversion compared to aqueous solvents:

- Water-lean solvents operate at lower temperatures, which inhibits the undesirable, endothermic reverse-water-gas-shift side reaction ($\Delta H° = 41.2$ kJ/mol) and enhances the desirable CO_2 hydrogenation reactions.
- The high CO_2 physical solubility of water-lean solvents enables CO_2 conversion at lower CO_2 pressure and temperature.
- Water-lean solvents promote CO_2 hydrogenation processes (e.g., to methane, methanol)) that produce water as a byproduct, where the excess water in aqueous solvents reverses the equilibrium and can also cause catalyst deactivation.
- Water-lean solvents are less susceptible to corrosion and decomposition.

2.2.3 CO_2 Compression and Transportation

Carbon capture and conversion can be implemented by (a) direct conversion of CO_2 to value-added products with a facility co-located with the CO_2 capture plant or (b) the development of integrated CO_2 networks connecting multiple sources and sinks (Al-Yaeeshi and Al-Ansari 2022). If the capture and conversion plants are not co-located (i.e., green H_2 is not available where CO_2 is captured), CO_2 can be transported from sources to sinks via pipeline. This is one of the most economic options (Lu et al. 2020). In this scenario, CO_2 enters the pipeline as a dense phase liquid, which requires much higher pressure, 15.3 MPa, and relatively low temperature, 30 °C (James et al. 2019). This can be achieved by a multi-stage centrifugal compressor with an intercooler between each stage. A dehydration unit is included to remove moisture from the CO_2 stream and allow safe transport toward the CO_2 sink, as wet CO_2 is extremely corrosive due to formation of carbonic acid. The CO_2 pipeline is similar to the natural gas pipeline, but the design and construction considerations are quite different due to the differences in gas compositions and transportation destinations.

If the CO_2 conversion plant is co-located with the capture plant, CO_2 compression is still required because the conversion usually happens at relatively high pressure (more than 15 bar), while CO_2 release from the capture unit is usually available near ambient or slightly higher pressure. In this case, a centrifugal compressor with fewer stages than the above case will be required to overcome the pressure difference. The number of stages depends on the selection of product (methane or methanol) and its required conversion pressure. Considerable electricity is needed for CO_2 compression due to the large pressure ratio between the capture and conversion units.

2.2.4 CO_2 Conversion

CO_2 can be turned into methane or methanol, which can be potentially used in existing Air Force facilities or converted to sustainable aviation fuel with more conversion steps. Choosing between methane and methanol as the final product hinges on whether the existing infrastructure or the targeting end users at the Air Force installation are geared towards gaseous or liquid fuels. Detailed discussion about the optimal use cases and scenarios is in Section 2.4.

The conversion can be done by reacting CO_2 with H_2 in the presence of special materials called catalysts (which make the conversion easier and faster). During the process, water is also created. This reaction releases heat and requires high temperature and pressure. There are many ways to turn CO_2 into methane and methanol by using different types of energy and substances, including thermal catalytic (thermal energy and a catalyst), electrochemical (electrical energy), photochemical (light/photon energy), plasma, and biological methods. These conversion technologies are rapidly evolving. Catalysts play a central role in all these technologies, and many catalysts have been developed to convert CO_2 efficiently and selectively into value-added products.

The market viability of these concepts depends on several factors, including capital costs, separation costs, and market demand. In most cases, the cost of producing clean hydrogen is the most important factor. Among these methods, thermal catalytic conversion is the most advanced in terms of technology readiness because it has already been demonstrated at large scales. Other methods are still in early stages of development. This discussion focuses exclusively on CO_2-to-methane and CO_2-to-methanol processes using thermal catalytic methods. Appendix A Section A.3 provides an in-depth description of catalyst development and other CO_2 conversion methods.

Methane: The chemical reaction turning CO_2 to methane by reacting with H_2 is called CO_2 methanation ($CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2\ H_2O$). This is a thermodynamically favorable reaction that tends to occur spontaneously without the need for external input of energy. Catalysts help the CO_2 and H_2 react more quickly and efficiently, resulting in mostly methane and not other unwanted products. If the hydrogen used in this process comes from renewable sources like solar or wind power, it is called a "power-to-gas" process. This means the whole system does not produce any carbon emissions.

Figure 2.3 shows a conceptual process flow diagram for a thermochemical CO_2 methanation process (Sun 2016). This process has one important challenge: the reaction releases a lot of heat, and the temperature must be kept under control. One way to do this is to use a special reactor system. Such systems have multiple reactors with intermediate cooling and gas recycling steps that are designed to keep the temperature low and avoid overheating. One example system is the commercially available Topsøe Recycle Energy-Efficient Methanation Process (TREMP) (Topsøe 2009).

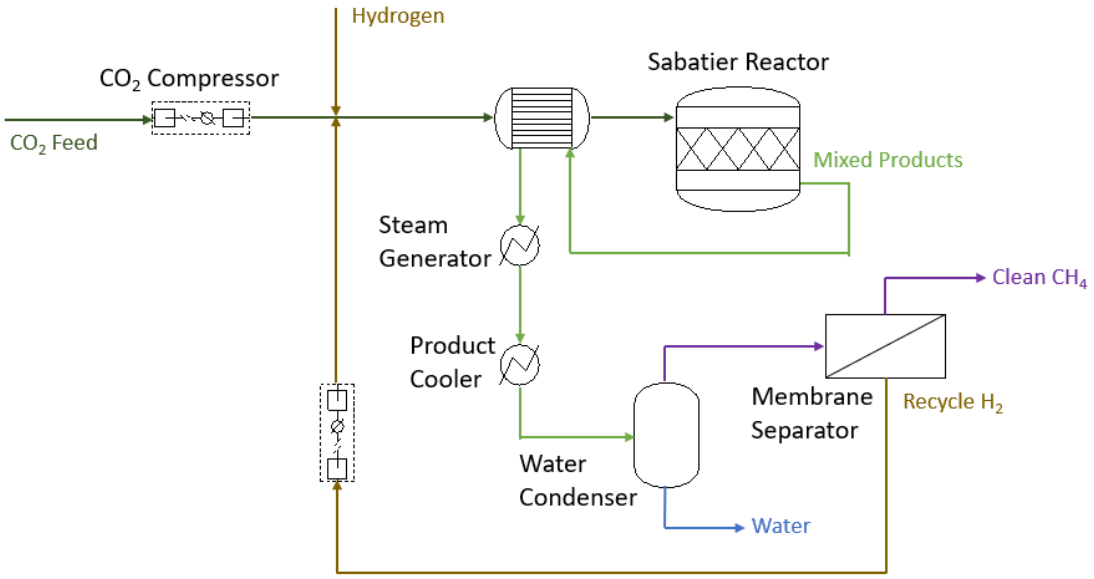

Figure 2.3. Simplified Process Flow Diagram for CO_2 Methanation

Methanol: Traditionally, methanol is made from a mixture of carbon monoxide (CO) and H_2 called syngas. This syngas often comes from fossil fuels or natural gas. The process happens under high pressure and temperature and requires special catalysts made of copper, zinc, and aluminum oxides. Scientists are now interested in using CO_2 instead of CO to make methanol. This reaction, called "CO_2 hydrogenation," combines CO_2 and H_2 to create methanol and water. When the electricity used to produce the H_2 comes from renewable sources like solar or wind power, the process is called "power-to-methanol." Just like the power-to-gas process, this method has a low carbon footprint. Three primary reactions occur in the reactor:

- $CO + H_2 \leftrightarrow CH_3OH$ ($\Delta H° = -90.7$ kJ/mol)
- $CO_2 + H_2 \leftrightarrow CO + H_2O$ ($\Delta H° = +41.2$ kJ/mol)
- $CO_2 + 3H_2 \leftrightarrow CH_3OH + H2O$ ($\Delta H° = -49.5$ kJ/mol)

Note: $\Delta H°$ represents the standard enthalpy (a thermodynamic property that represents the total heat content of a system) change in a chemical reaction. A positive $\Delta H°$ indicates that a reaction is endothermic, meaning it absorbs heat from the surroundings, while a negative $\Delta H°$ indicates that the reaction is exothermic, releasing heat to the surroundings.

Unlike CO_2 to methane, CO_2 to methanol is an equilibrium-limited reaction, where reactions can process in both directions and neither direction is strong enough to completely drive the reaction one way. This means there will always be some reactants and products present at equilibrium. Therefore, catalyst development, optimization of reaction conditions (concentration, temperature, and process that impact reaction equilibrium) and low-cost separation between reactants and products are crucial steps for successful deployment of this technology. Several ways to turn CO_2 into methanol have been tested on a small scale. Since 2011, Carbon Recycling International (CRI) has been operating the first CO_2-to-methanol plant on an industrial scale. Figure 2.4 shows a simple version of this process, which involves a main reactor, gas separation, recycling of unconverted reactants, and product purification (Atsonios et al. 2016).

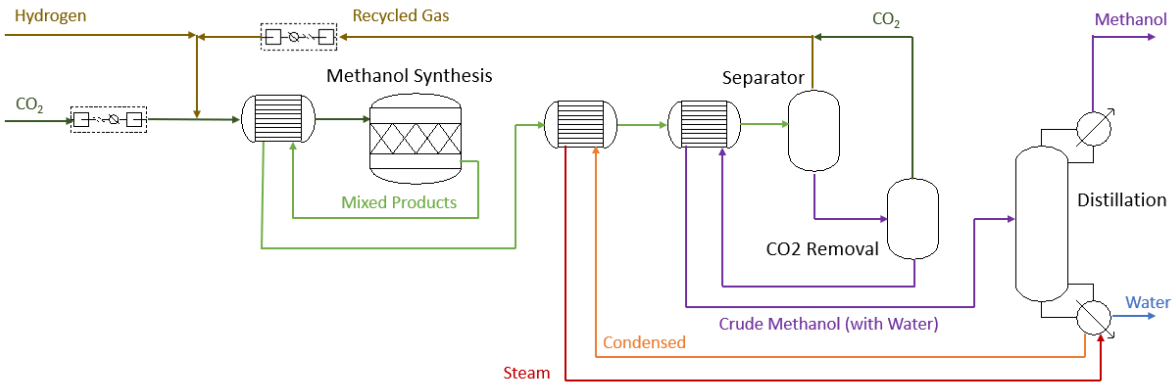

Figure 2.4. Simplified Process Flow Diagram for CO_2-to-Methanol Conversion

2.2.5 Supply of Renewable H_2

Production of CO_2-derived products plays a significant role in disconnecting fossil resources from the economy's needs and improving system resilience. CO_2 hydrogenation ($CO_2 + H_2 \rightarrow X$) is one of the most readily available conversion pathways to produce value-added fuels or chemicals, such as methane and methanol, but it consumes large amounts of H_2 as intermediate material and energy sources.

The environmental benefits of converting CO_2 to methane and methanol depend heavily on the source of the hydrogen used in the process. Currently, most hydrogen (96%) globally comes from fossil fuels like natural gas, oil, and coal, creating significant GHG emissions (Howarth and Jacobson 2021). This type of hydrogen is called "grey" and cancels out the environmental benefits of capturing and using CO_2. Only a small amount of hydrogen (4%) comes from water electrolysis using renewable energy like solar, wind, or hydro power. This "green" hydrogen has a near-zero carbon footprint and is ideal for clean CO_2 conversion. Another promising option is "blue" hydrogen, which is produced using fossil fuels but integrated with carbon capture as discussed in Sections 2.2.1 and 2.2.2 to trap CO_2 generated during hydrogen production. This captured CO_2 can then be used in the CO_2 conversion process. However, there are currently no commercial blue hydrogen plants in operation. If not used on-site, once produced, hydrogen needs to be converted for storage and transportation due to its low energy density. Liquid hydrogen, compressed hydrogen gas, or hydrogen carriers like ammonia and metal hydrides can be used for this purpose. For more details on H_2 production, supply chain, and resilience considerations, see the Emerging Technology Review: Hydrogen Production and Storage (Briggs et al. 2023).

2.3 Configuration Options

When assembled together, all components described in Section 2.2 form a conventional configuration for carbon capture and conversion, as illustrated in blue in Figure 2.5. In this configuration, the captured CO_2 is collected at near ambient pressure, then compressed and transported for either (a) conversion to produce value-added products or (b) permanent storage underground. This option is neither energy-efficient nor cost-effective, as shown in Figure 2.5.

An alternative configuration option using integrated CO_2 capture and conversion technologies addresses this challenge. As shown in the route marked in green in Figure 2.5, the captured CO_2 in the solvent is converted directly to value-added products in the capture medium, bypassing the energy-intensive solvent regeneration (CO_2 collection), compression, and transportation steps (Figure 2.5) (Heldebrant et al. 2022). Thus, in the integrated CO_2 capture and conversion approach, value-added products (gas, liquid, or solid) are moved from the capture site instead of compressed supercritical (substance with properties that are intermediate between those of a gas and a liquid) CO_2. Further, selling CO_2-derived value-added products could offset some of the cost of CO_2 capture, offering a strong incentive for commercialization. In addition, the entire carbon capture and conversion plant can be more intensified, requiring less equipment, which can fit for certain DAF facilities with limited space available for new technology installation.

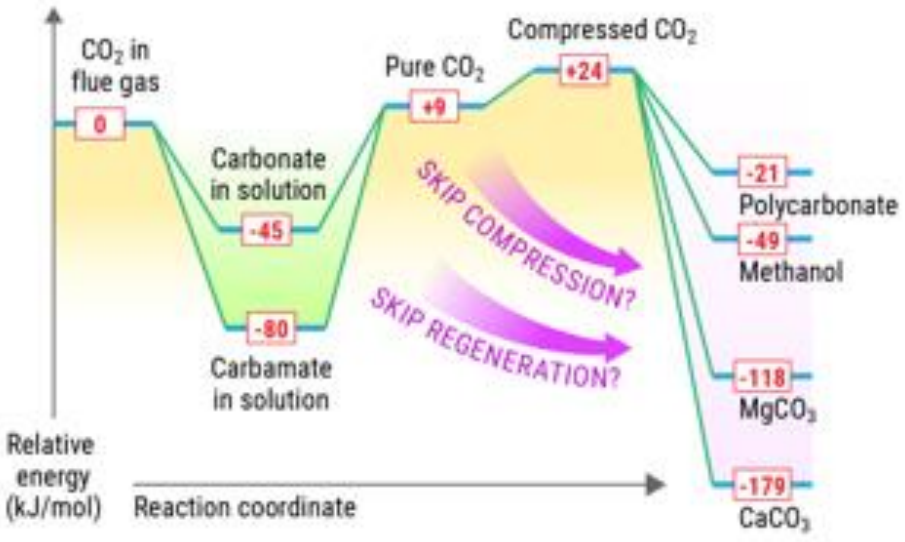

Figure 2.5. Energy Comparison between Traditional and Emerging Integrated CO_2 Capture and Conversion Approach (Heldebrant et al. 2022)

Figure 2.6 and Figure 2.7 show the proposed configurations for the integrated carbon capture and conversion to methane and methanol processes, respectively. Technical details can be found in Appendix A, Section A.4.

Integrated capture and conversion to methane: In this process, EEMPA, a special single-component water-lean solvent, is used to first capture CO_2 from flue gas. Then, the CO_2-rich solvent is mixed with H_2, processed with a special catalyst at low temperature (less than 200 °C) and converted to methane. The reaction happens in liquid form, which reduces the energy needed to compress the CO_2. Additionally, the heat generated by the reaction is used to partially offset the energy needed to regenerate the capture solution. In addition, the process is operated at temperatures that are less than half that of traditional CO_2-to-methane method, making it more efficient and cost-effective.

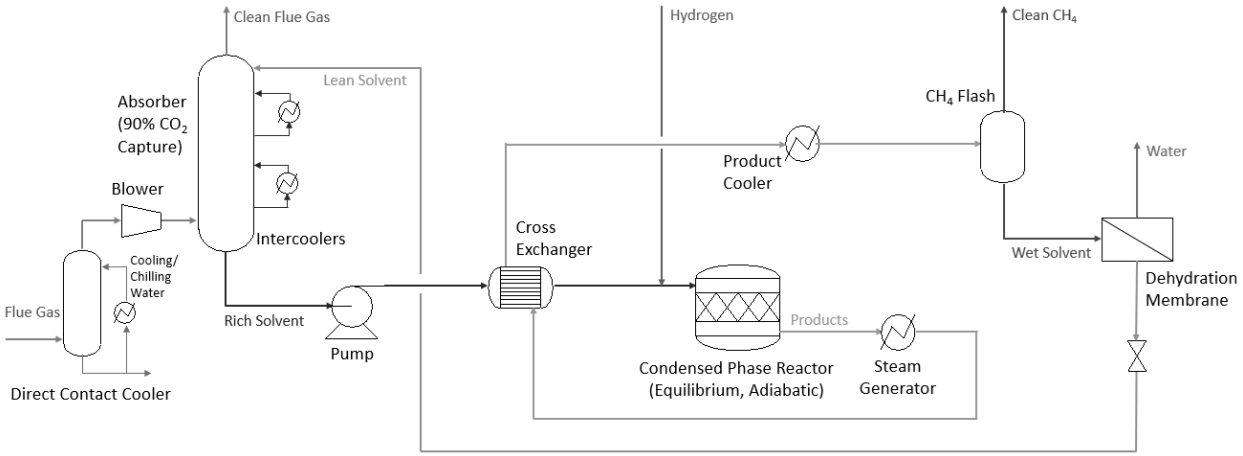

Figure 2.6. Simplified Process Flow Diagram of the Integrated Carbon Capture and Conversion to Methane Process

Integrated capture and conversion to methanol: The CO_2 capture step is the same as the above process. Here, the CO_2-rich solvent that exits the absorber is then heated, compressed, and fed to the main reactor with H_2 to produce methanol. The amount of inlet H_2 for the reactor exceeds the theoretical reaction requirement in order to shift the reaction equilibrium, which favors the CO_2 conversion. After the reaction, the excess H_2, in the gas phase, is then separated in a low-temperature flash drum before being recycled back into the reactor. Methanol, CO_2-lean solvent, and water constitute the liquid phase product from the H_2 recovery drum. The non-volatile lean solvent is recovered in flash drums at a lower pressure and recycled back into the CO_2 absorber. The methanol/water mixture is then routed to a distillation column to produce high-purity methanol.

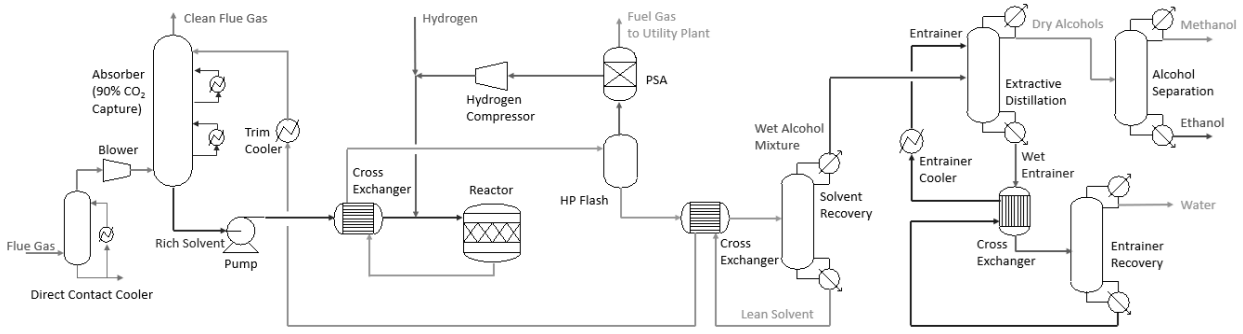

Figure 2.7. Simplified Process Flow Diagram of the Integrated Carbon Capture and Conversion to Methanol Process

2.4 Optimal Use Cases and Scenarios

The value of these technologies to DAF is their ability to address real-world challenges and practical uses. This section explores the diverse use cases and scenarios across industries and how these technologies can shape a resilient and low-carbon future for DAF. There are four potential products that can be made with captured CO_2:

- Methane as energy source
- Methanol as energy source or for chemical production

- Sustainable aviation fuel (from methanol)
- E-fuels (methane or methanol as energy carriers for renewables).

Direct use of methane: Methane is the simplest hydrocarbon, and as the main component of natural gas is one of the cleanest burning fossil fuels in terms of carbon and other emissions. Methane is also a potent GHG with ~25 times the 100-year radiative forcing (i.e., warming) power of CO_2. Renewable methane [also referred to as renewable natural gas (RNG) and synthetic natural gas (SNG)] produced from the CO_2 capture and utilization technology can be used most obviously to replace current fossil natural gas, fuel oil, diesel oil, or coal in boilers and furnaces at a centralized heat plant. If replacing natural gas, the RNG or SNG made from CO_2 can be directly dropped into the existing gas-fired infrastructure with few or no equipment retrofits. If it is used to replace other fossil solid or liquid fuels, retrofits may be needed.

In the context of DAF installations, RNG or SNG can be an energy storage medium, readily available to power vehicles and facilities. Moreover, integrating RNG or SNG into operations decreases reliance on conventional fossil fuels, thereby mitigating potential vulnerabilities linked to traditional fuel supply chains. RNG produced from CO_2 could potentially be used in gas turbines to generate prime power or backup power (Thomas et al. 2023). It may also be worth considering using the methane as a more practical and safe hydrogen carrier for onsite storage and using hydrogen for energy production.

Direct use of methanol: Methanol is one of the most common organic chemicals produced and has many uses in the marketplace. It is a versatile compound that can be used directly or as an intermediate feedstock for conversion to many other chemicals and fuels. In the context of DAF installations, methanol may be practically limited to use as (1) a fuel source for heat and/or power to replace diesel, fuel oil, or natural gas combustion; or (2) a feedstock for further conversion into sustainable aviation fuel. Methanol is used to produce the gasoline additive MTBE (methyl tert-butyl ether) and has also been used as transportation fuel in internal combustion engines in the U.S. and globally in high gasoline blends (in flexible fuel vehicles) and lower gasoline blends (in unmodified engines). However, it has a lower heating value (amount of heat energy produced when it is completely burned per unit of fuel) than hydrocarbon fuel and is not currently used as a replacement for vehicle transportation (other than additive MTBE) to any significant extent in the United States. Methanol can also be converted into renewable dimethyl ether, which has a higher cetane number (a measurement of the quality of diesel fuel; the higher the number, the better the fuel burns within the engine of a vehicle) and is less toxic than petroleum diesel (Matzen and Demirel 2016). This may be of interest to future DAF efforts to decarbonize the installation fleet.

While methane product is the obvious candidate for heat and power substitution since it can be directly dropped into a gas turbine combustion unit, methanol can also be combusted in gas turbines or boilers with some retrofits (ADI Analytics 2017). While the economic and environmental tradeoffs of methanol versus methane should be considered, methanol is touted as having advantages with respect to emissions, heat rate (rate of temperature change over time), and efficiency (Methanol Institute 2023). As a liquid, it is easy to store and transport and may also bring advantages in terms of GHG emissions compared to methane, which as a gas is inherently more prone to leakage. Methanol could also be used in fuel cells (electrochemical device that generates electricity through a chemical reaction between a fuel and oxygen/air) for site power generation.

Intermediates for sustainable aviation fuel production: There has been significant interest in sustainable aviation fuel over the past few years, fueled by the current Administration's sustainable aviation fuel Grand Challenge (DOE 2023) and the aviation industry's commitment to reach net zero carbon emissions by 2050 (IATA 2023). Methanol is a good intermediate for fuel production because it can be efficiently converted to fuel with commercially available technology, and it is easier to manage and store compared to potential sustainable aviation fuel gas-phase intermediates like methane. Several commercial entities have developed methanol-to-jet technology with planned demonstration plants in the works, including but not limited to Topsøe, Nacero (PR Newswire 2023), ExxonMobil, and Honeywell UOP. Converting methanol to jet fuel requires three additional main processing steps: (1) converting methanol to light olefins; (2) oligomerizing light olefins to longer **sustainable aviation fuel** -length olefins; and (3) a final hydrogenation step to produce hydrocarbon blendstock fuel. RNG or SNG produced could also be used as an intermediate to produce fuel for ground or aviation fleets via various synthesis methods such as Fischer-Tropsch (a series of chemical reactions that converts syngas into liquid hydrocarbons) (Tarka et al. 2021), although this may be a less efficient way to make jet fuel compared to other intermediates such as methanol. Accordingly, a CO_2-to-jet-fuel project will require higher capital investment and operating cost compared to a CO_2-to-methanol or a CO_2-to-methane project but may be warranted given the value of sustainable aviation fuel versus methanol or methane for Air Force application.

Energy storage or carrier for renewable electricity / hydrogen: Due to the storage and transportation challenges of renewable electricity and hydrogen, methane and methanol produced from CO_2 and renewable H_2 (also known as e-fuels) can be considered a promising alternative by using the existing infrastructure of fossil-based natural gas and methanol. E-fuels can provide a low-cost grid-balancing solution for renewable penetration (Becker et al. 2019).

3.0 Technical Considerations

Carbon capture and conversion involves many different components, as reviewed in Section 2.2. For each component, various technologies are available but at different stages of maturity. This section discusses factors that limit the adoption of the carbon capture and conversion technologies, including component availability, supply chain issues, and limited full-scale demonstrations.

3.1 Limiting Factors and Constraints (other than siting characteristics)

The key limiting factors for widespread adoption of carbon capture and conversion are green H_2 availability, manufacturing of new materials (i.e., solvents, sorbents, catalysts, membranes, etc.), and large-scale deployment. This technology often relies on green H_2 as a key reactant and energy source, but the current production of H_2 is dominated by fossil fuels, negating the environmental benefits of carbon capture and conversion. In addition, green H_2 is currently more expensive than H_2 derived from fossil fuel, creating cost disparity. Some of the carbon capture and conversion technologies, especially those claiming low energy consumption, use materials that are not commodity products in the current market. It is important for near-term technology deployment to find vendors that can manufacture these new materials and develop market demand. Moreover, limited large-scale demonstration may potentially create uncertainty in technological performance at scale and high upfront capital investment.

These limiting factors and constraints are manageable with concerted effort from stakeholders, such as government support, public-private partnerships, industry engagement, public engagement, and education.

3.2 Technical Maturation

Carbon capture and conversion is a promising technology for mitigating climate change. The current state of technology maturation varies across different components of the process. For each key component in the carbon capture and conversion process (Figure 2.1), there are technologies that have achieved high maturation and have been demonstrated in pilot projects at commercial scale. The DAF can consider these successful technologies for near-term installation.

In this report, technology readiness level (TRL), a measurement widely used in industry and government-funded research and development (R&D) programs, is used to describe the maturity of carbon capture and conversion technologies. Figure 3.1 provides a high-level description of each TRL.

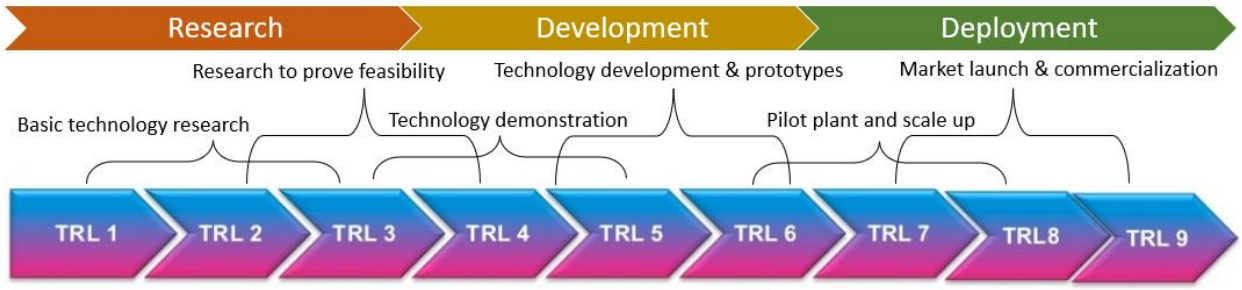

Figure 3.1. Description of Technology Readiness Levels

3.2.1 Current State of Technology Development

As discussed in Section 2.0, several technologies are available for each core component in the supply chain of carbon capture and conversion to methane and methanol, but at different TRLs. Table 3.1 summarizes the TRLs of leading technologies for CO_2 capture and CO_2 conversion (Hong 2022), of which detailed technology description can be found in Appendix A. Technologies for H_2 production are detailed in another report to AFCEC focusing on H_2 (Briggs et al. 2023). Here, technologies at an early R&D stage with TRLs below 3 are excluded. As shown in Table 3.1 (Hong 2022; Dziejarski et al. 2023), at least one commercially available technology (TRL of 8 or higher) is available for each core component in the entire carbon capture and conversion process. There are also emerging technologies with much lower estimated cost and energy consumption and a TRL between 4-6 (proven at lab or pilot scale).

Table 3.1. TRLs of Technologies for Carbon Capture and Conversion to Methane and Methanol

Component	Technology	TRL
Post-combustion CO_2 capture	Aqueous amine solvents (power plant)	8
	Water-lean solvents	5
	Dense inorganic membrane	3
	Polymeric membrane (power plant)	6
	Temperature swing adsorption	7
	Cryogenic	5
CO_2 transportation	Onshore and offshore pipelines	9
	Ships	8
CO_2 conversion	CO_2-to-methanol (conventional thermal catalytic)	8
	CO_2-to-methane (conventional thermal catalytic)	8
	CO_2-to-methanol (integrated capture & conversion)	4
	CO_2-to-methane (integrated capture & conversion)	3

3.2.1.1 Successful Pilots or Demonstrations

Carbon capture and conversion is an emerging technology that has not been fully commercialized, and therefore, it has not been installed at DAF or similar facilities. However, with new and updated carbon policies (i.e., 26 U.S. Code § 45Q,[1] President Biden's Bipartisan Infrastructure Law) to promote a net-zero emissions economy, numerous R&D, scale-up, and demonstration projects are being conducted to investigate and advance the TRLs of alternative carbon capture and conversion technologies with low cost and low energy consumption. Some scale-up (the process of increasing the size or capacity of a system) projects are shown in Figure 3.2 and Table 3.2 and are discussed below.

Carbon capture: To accelerate the scale-up of emerging carbon capture technologies, the U.S. Department of Energy (DOE) and Southern Company Services built and continue the operation and maintenance of the National Carbon Capture Center in Wilsonville, Alabama, to offer third-party technology evaluation at bench and pilot scales. Another world-class carbon capture testing facility is Norway's Technology Center Mongstad, which since 2019 has successfully tested CO_2 capture technologies developed by Aker Solutions (Norway), Alstom SA (France), Cansolve Technologies Inc. (Canada), Carbon Clean Solutions (UK/India), ION Engineering (USA), and Fluor Corporation (USA) (TCM 2023). In addition to pilot testing, several demonstration projects are underway in the U.S. For example, as of August 2019, the NRG Energy Petra Nova project in Houston had captured over 3.27 million short tons of CO_2 from a coal-fired power plant and sent it for enhanced oil recovery (DOE 2019).

CO_2 to methanol: Before 2020, Iceland's George Olah was the largest CO_2-to-methanol plant in operation, converting 5,600 metric tons per annual (Mtpa) CO_2. This plant uses CRI's CO_2 conversion technology and green H_2 produced from renewable electricity. More recently, a commercial-scale plant was built in Anang, Henan Province, China, using the same technology but different CO_2 and H_2 resources. In November 2022, this facility became the world's first commercial-scale CO_2-to-methanol plant. The plant was designed with a carbon capture capacity of 160,000 Mtpa and a methanol production capacity of 110,000 Mtpa. The plant captures CO_2 from lime production emissions and recovers H_2 from coke-oven gas. This is an important industry milestone toward a net-zero economy. Another commercialization project in China using CRI's technology is expected to come online in 2023 (PR Newswire 2022).

CO_2-to-methane: A number of CO_2-to-methane (power-to-gas) demonstration plants were built under the European research project STORE&GO. Since January 2019, the first power-to-gas demonstration plant in Falkenhagen, Germany, has been producing and feeding SNG to the natural gas grid. This plant produces up to 1,400 m^3 of SNG per day and achieves over 700 operational hours with a CH_4 purity above 99% (Graf 2019). Green H_2 from renewable electricity and CO_2 from a bioethanol plant are used as the feedstock.

Table 3.2. Pilot- and Large-Scale CO_2 Conversion Projects

Product	Company (or Project) / Location	Capacity	Reference
Methanol	Carbon Recycling International / Iceland	5,600 CO_2 Mtpa	IEA 2020
Methanol	Carbon Recycling International / China	160,000 CO_2 Mtpa	PR Newswire 2022
Methane	STORE&GO / Germany	1,400 m^3 SNG /day	Graf 2019

[1] The text for 26 U.S. Code § 45Q (credit for carbon oxide sequestration) is available at https://www.law.cornell.edu/uscode/text/26/45Q.

Methane	ETOGAS GmbH / Germany	6 MW	Reuters 2018

3.2.2 Market Penetration

According to the Global CCS Institute (2021), there are 135 commercial carbon capture and sequestration (CCS) projects in the project pipeline, of which 58 are in advanced development, 4 are in construction, and 27 are in operation (Table 3.3). The United States leads the activity, and success demonstrates convincingly that where policy creates a business case for investment, projects proceed. Other leading countries are Belgium, the Netherlands, and the United Kingdom. As of 2021, about 35 million metric tons of CO_2 are captured per year. Figure 3.2 shows a rapid market penetration of carbon capture to different industrial sectors with a growing number of projects and growing project scales in million Mtpa basis.

Table 3.3. Commercial CCS Facilities by Number and Total Capacity in 2021

	Operational	In Construction	Advanced Development
Number of facilities	27	4	58
Capture capacity	36.6	3.1	46.7

Most of the pilot- or large-scale CO_2-to-methane (or power-to-gas) plants are located in Germany and use the most mature thermal catalytic technology for conversion (TUVSUD 2019). According to an evaluation from Ludwig-Bölkow-Systemtechnik GmbH (Oberst 2023), this technology is advancing toward maturity. Currently in Germany, 50+ plants with a 55-MW total electric capacity are in operation or are planned. Large projects with three-digit megawatt capacity have been announced. The natural gas shortage and the high penetration of renewable electricity in the local grid may contribute to the rapid market penetration of CO_2 to methane in Germany.

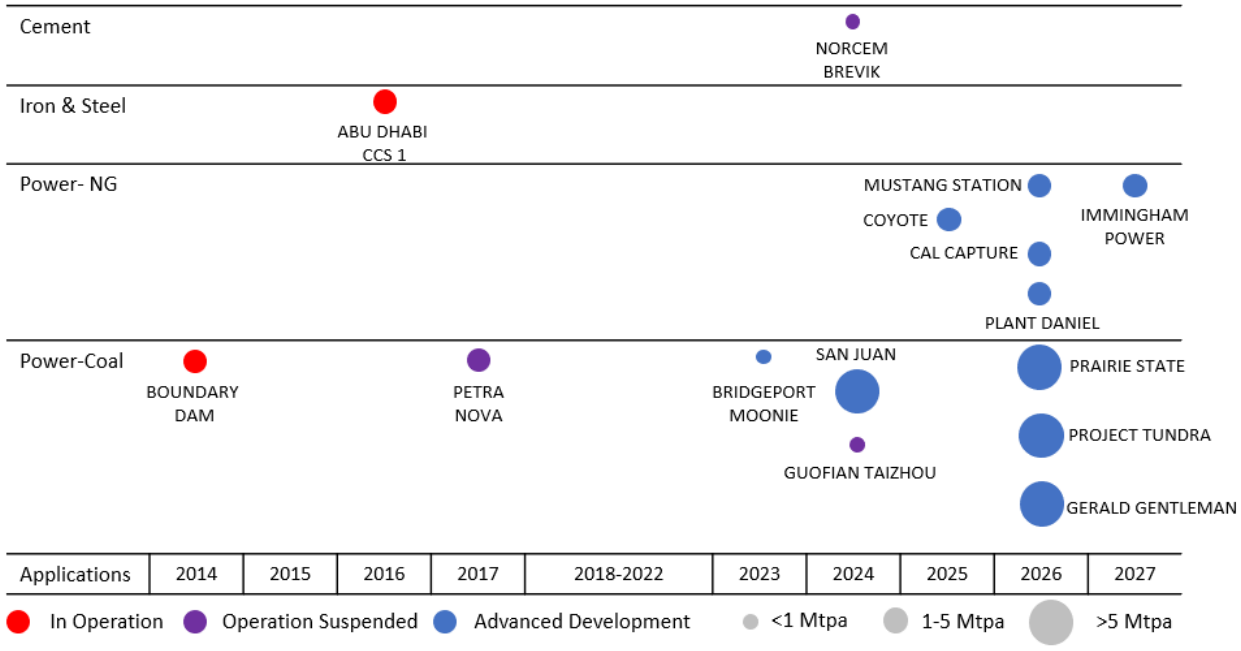

Figure 3.2. Post-combustion CO_2 Capture Projects by Sector and Scale

3.2.3 Key Challenges and Barriers to Adoption

Even though multiple high-TRL technologies are available for CO_2 capture and conversion, multiple challenges limit industrial adoption (Howard 2022), as described below.

- **Cost and business model**: All high-TRL technologies carry high operating and capital costs, which add to the cost of doing business but offer few opportunities for revenue generation. Federal tax credits help offset the high cost but not for all emitters.
- **Infrastructure development**: If CO_2 and H_2 are not available at the same location, carbon capture and conversion to methane and methanol will require infrastructure for CO_2 and/or H_2 transportation. Timing of development will impact the construction of needed infrastructure.
- **Material manufacturing**. Materials, such as solvents, sorbents, and catalysts, used in these emerging CO_2 capture and conversion technologies are not commodity products and are not available in large scales. Scaling up the production of these critical materials is important for technology deployment.
- **Access to green H_2**: Currently, about 95% of H_2 is produced from fossil energy globally, with high carbon footprint (Gencer 2021). Due to the high cost of CO_2-to-methane/methanol technology, use of green H_2 in the conversion stage is necessary to gain tax credits and establish a feasible business model. Therefore, the adoption of CO_2 conversion to methane/methanol highly depends on the market penetration of green H_2.

To overcome these challenges, most recent technology development has focused mainly on the following:

- Material development: scientific projects are focusing on low cost, high CO_2/N_2 selectivity, high CO_2 uptake, high durability, and low maintenance
- Catalyst development: scientific projects are focusing on high conversion, high selectivity, high activity, minimum deactivation, and long lifetime
- Process optimization: low operating and capital costs
- Scale-up and de-risking
- Business model development with policy support

Several policy options are also being considered, such as modifying existing incentives, encouraging community engagement, standardizing life cycle assessment guidelines, and developing technology-neutral standards.

Note that the above challenges and barriers are applicable to installing carbon capture and conversion in existing facilities that burn fossil fuels. For DAF installation, in-house training for operation, maintenance, and regulatory requirements is highly recommended, as is supervision by experts in chemical engineering because operating a carbon capture and conversion plant exceeds the common practice of DAF.

4.0 Regulatory Overview

This section details the regulatory approvals required to demonstrate carbon capture and conversion technology.

4.1 Federal Requirements

Construction and operation of a facility that captures and converts CO_2 to methane or methanol will require coordination with federal, state, and local governments regarding pertinent environmental laws and regulations. The permitting process and regulatory requirements should be broadly typical of any manufacturing facility and involve measures to protect and preserve public health and our nation's air and water quality, wildlife, and historic sites. In addition to the summaries provided here, the White House Council on Environmental Quality Report (CEQ 2021) provides a good overview of applicable federal permitting information and resources for carbon capture, utilization, and sequestration projects.

The following subsections discuss the major governing federal laws and regulations and associated requirements for manufacturing facilities. These may apply to carbon capture and methane/methanol production plants, but the specific mix of regulatory requirements will be highly dependent on the details and location of the project. Note that this section focuses on the federal requirements, rules, and guidance potentially applicable to a manufacturing plant that captures and converts CO_2 to methanol or methane. Regulations specific to transportation (e.g., pipeline) and geologic storage of CO_2 are not covered here.

4.1.1 Clean Air Act

CO_2 capture and conversion facilities are subject to the strict regulations under Title V of the 1990 amendments to the Clean Air Act (CAA) to obtain a Title V Operating Permit due to their potential emissions. If the air pollutant emissions exceed the thresholds listed in Table 4.1, they qualify as "major sources" and require comprehensive permits outlining emission limits, monitoring, and reporting measures (EPA 2023a). Each state must issue Title V permits outlining air pollution control requirements for major emitter. These permits, typically issued by state/local governments detail the following: permitted activities, emission units, control devices, applicable limits, monitoring, reporting, and certification methods. Facilities must identify and comply with the most stringent local, state, and federal regulations.

Table 4.1. Lower Major Source Thresholds for Nonattainment Areas[(a)]

Non-attainment Area Designation	VOC or NOx	CO	PM-10
Marginal	100 tons/year		
Moderate	100 tons/year	100 tons/year	100 tons/year
Serious	50 tons/year	50 tons/year	70 tons/year
Ozone transport region (other than severe or extreme)	50 tons/year (VOC only)		
Severe	25 tons/year		
Extreme	10 tons/year		

(a) Data are from https://www.epa.gov/title-v-operating-permits/who-has-obtain-title-v-permit
VOC = volatile organic compound

In addition, carbon capture and conversion plant may require pre-construction New Source Review (NSR) permits. The stringency of permit increases in nonattainment areas (not meeting air quality standards). See EPA resources[1,2,3] for details. Depending on which carbon capture and conversion technologies is selected for implementation, extremely hazardous substances may be involved, such as amines, methane, hydrogen, etc., which require a risk management plan according to Section 112(r) of the CCA. The risk management plan must include a hazard assessment, prevention program, and emergency response program. More information on the risk management plan and the list of regulated substances can be found on the EPA website.

4.1.2 Clean Water Act

The Clean Water Act National Pollutant Discharge Elimination System (NPDES) permit program was established in 1972 to protect the nation's waters by regulating water pollution discharge point sources. A point source is "any discernable, confined and discrete conveyance, such as a pipe, ditch, channel tunnel, conduit, discrete fissure, or container."[1] If a facility will discharge to a municipal sewer system, then typically a permit from the state/local authority will be required that includes water quantity and pollutant discharge limits and sampling and monitoring requirements that enable the authority to meet their NPDES permit limits. The permit will contain effluent limitations based on EPA guidelines and standards and will consider the technology available to control pertinent pollutants and the current quality of the receiving water. Individual sets of guidelines have been established for many industrial SIC (Standard Industrial Classification) categories.[2] The list includes certain subsectors of the Organic Chemicals, Plastics, and Synthetic Fibers category, including SIC 2869, Industrial Organic Chemicals, Not Elsewhere Classified.

Upon initial investigation, it seems plausible that a facility capturing and converting CO_2 to methane or methanol may fall under this category, and if so, the guidelines established for this category[3] would apply and be incorporated into the NPDES permit. The guidelines have been

[1] https://www.epa.gov/npdes/npdes-permit-basics
[2] https://www.epa.gov/eg/industrial-effluent-guidelines
[3] https://www.ecfr.gov/current/title-40/chapter-I/subchapter-N/part-414

established by EPA considering a wide range of pollutants, including toxic, conventional, and non-conventional. The list of 126 toxic, or "priority," pollutants is specified in 40 CFR Part 432, and is available on the EPA website.[1] The conventional pollutants include biochemical oxygen demand, total suspended solids, fecal coliform,[2] pH, and oil and grease (EPA 2023c). Non-conventional pollutants do not fall under either of the previously mentioned categories and may include, for example, chemical oxygen demand, total organic carbon, nitrogen, and phosphorus (DOI 2023). For a carbon capture and conversion plant, biochemical oxygen demand and total suspended solids are the primary water pollutants.

4.1.3 Emergency Planning and Community Right-to-Know

Tier I and II reporting[3] may be required under the Emergency Planning and Community Right-to-Know Act for facilities that use, store, and release certain chemicals (i.e., solvents used in carbon capture unit). If the facility is required to maintain safety data sheets under OSHA regulations, then it is required to report.

4.1.4 Title 41 of the FAST Act

The 2015 Fixing America's Surface Transportation (FAST) Act was created to support long-term funding for transportation infrastructure planning and investment in the U.S. The FAST Act streamlined the permitting process for certain types of infrastructure projects, including carbon capture, utilization, and sequestration. The Act also formed the Federal Permitting Improvement Steering Council, which is responsible for environmental reviews and permitting of qualifying projects (Federal Infrastructure Projects 2023). The regulations and permits discussed earlier would still apply, but the program, referred to as "FAST-41," supports a more timely, predictable, and transparent process for applicants than the standard review process.

4.2 State and Local Regulatory Activity

Additional state or local regulations, requirements, or permits may also apply depending on the details of the project, local regulations and land use, and other factors. Rules administered by states and local governing bodies may differ from the federal rules but in general must be at least as stringent as the federal rules. EPA advises projects to consult with their local EPA regional office for further guidance.

[1] https://www.epa.gov/sites/default/files/2015-09/documents/priority-pollutant-list-epa.pdf

[2] Fecal coliform are bacteria that are used as indicators of water quality; the presence of fecal coliform in water can indicate a potential risk of harmful pathogens and may signal the need for further water treatment and purification.

[3] Tier I reporting: initial level of reporting required under the Emergency Planning and Community Right-to-Know Act. Tier II reporting: comprehensive level of reporting, providing more detailed information about hazardous chemicals

5.0 Risks

Construction and operation of carbon capture facilities have various risks and challenges. The following sections provide a detailed discussion of potential risks and challenges in building and operating carbon capture facilities and corresponding mitigation strategies.

5.1 Specific Carbon Capture Risks

The following challenges are ordered from most significant to least.

Cost risk: Construction of a carbon capture plant requires significant capital investment for purchasing capture equipment, installing pipelines, installing a storage tank, and providing power supply infrastructure, among other expenses. The overall cost depends on the selection of capture technologies, the source of CO_2, and the usage or storage of captured CO_2. Despite several technologies completing pilot-scale tests, they often lack commercial verification. This lack of verification may cause unforeseen challenges that create economic risks during the construction phase. Starting with a small-scale plant could significantly reduce the cost risks, offering valuable insights for future large-scale plant construction and operation.

Policy and compliance risks: As discussed in Section 3.2.3, CO_2 capture and conversion technology is cost-intensive and requires federal tax credits to help to offset the financial burden. Changes in the energy market or government policies can impact both the economic feasibility and the DAF's capacity to achieve carbon reduction objectives. To address policy and compliance challenges, it is essential to conduct uncertainty analyses for carbon projects before construction, actively engage with regulatory authorities, and seek legal counsel.

Evolving technology risk: Because of the ongoing and rapid progress of research on carbon capture and conversion, the cost of building a plant may be significantly reduced in the future. Related to this, building a capture plant using a currently mature technology might lead to economic challenges as more advanced technologies emerge. To address this, approaches such as assessing carbon capture technologies before making a selection, designing a flexible operational facility capable of operating at various scales, and building facilities that are easy for retrofitting could reduce the technology risks in the future.

5.2 Environmental Considerations

Although carbon capture facilities provide a positive environmental impact by reducing GHG emissions, the construction and operation of the carbon capture facility emits gas, wastes, water, and chemicals to its surrounding environment, which may lead to environmental contamination. These potential environmental impacts should be thoroughly addressed and mitigated during the project environmental review and permitting process. The following is a summary of these environmental considerations.

5.2.1 Environmental Impacts

Water supply: As discussed in Section 2.2.4, the CO_2 utilization techniques use H_2, generated from water for methane or methanol production. The carbon capture process that relies on water may compete with other local water needs, such as agriculture, municipal water supply, or ecological requirements. In regions facing water shortages, the increased demand for water by

a carbon capture plant can exacerbate existing challenges. To reduce the potential for water supply challenges, it is essential to assess local water availability and optimize the capture process to minimize water usage.

Waste disposal: The carbon capture technologies, such as MEA, Shell Cansolv, and PNNL EEMPA (Section 2.2.2), use water and organic solvents in the system. The wastewater from these technologies contains trace amounts of organic solvent. Also, in these processes, the organic solvents generate byproducts, which need to be removed from the process. The wastewater and byproducts may harm aquatic life and affect water quality. To minimize the process's environmental impact, a waste treatment system is necessary for the carbon capture plant. Similarly, other carbon capture and CO_2 conversion technologies involve disposal of hazardous solids (such as spent solid sorbent, spent catalyst), which need to be carefully handled.

5.2.2 Environmental Risks and Hazards

Environmental risks and hazards associated with a carbon capture plant include the potential leakage of a CO_2 product and the exposure or leakage of chemicals. Leakage of CO_2, a GHG, can contribute to environmental and climate-related impacts. Additionally, chemical exposure or leakage has the potential to contaminate soil, water, and air, impacting both terrestrial and aquatic environments. To prevent environmental contamination, it is crucial to implement comprehensive environmental impact assessments, robust safety protocols, adherence to regulatory standards, and ongoing monitoring and reporting. These measures are essential for the sustainable operation of the carbon capture plant.

In summary, like most emerging technologies, risks are involved in building and operating a carbon capture plant. For the DAF, a solution is to start by building a small-scale plant and having a dedicated team throughout the process focused on addressing and providing solutions for the risks.

5.3 Social Considerations

A successful installation of a carbon capture and conversion plant requires early and continual engagement and transparent communication with the installation's onsite personnel and their families, the public, and other stakeholders throughout the life of the project. As mentioned in Section 9.0, Recommendations and Path Forward, as with any newer technology, it is ideal to determine the plant's feasibility through a pilot- or demonstration-scale project in which any environmental and social considerations can be carefully monitored and documented before implementing at a large scale. This approach can enable any potential environmental issues (as outlined in Section 5.2) and any potential social considerations, as outlined below, to be documented and addressed before full and wide-scale adoption. Details about potential social considerations and community acceptance of implementing carbon capture and conversion technologies can be found in several open-access publications (Nielsen et al. 2022; Buck 2021).

5.3.1 Human Health Risk

Potential human health impacts may arise from chemical exposure, air emissions, hazards, water and land concerns, and quality of life issues, including noise, odor, and safety in the surrounding community. Depending on specific carbon capture and conversion technology used, solvents, catalyst, and other chemicals might pose risk of irritation, burns, or toxicity if exposure occurs. Some technologies using amine-based solvents can generate nitosamines, known carcinogens. Leaked CO_2 can acidify water bodies and harm local ecosystems, potentially impacting food and water sources. To reduce the human health risk, it is critical to monitor and control factors that influence such risks, such as emissions, noise, and chemical leakage. Additionally, designing robust safety protocols, adhering to safety standards, and establishing emergency response plans are essential approaches to reducing risks to human health for those working in the plant.

5.3.2 Social Impact

Construction and operation of a carbon capture and conversion plant may disrupt local communities and raise concerns about land use and its impact on local ecosystems. The plants require significant land for construction, including the plant itself, pipelines for transporting, and storage facilities for raw materials and final products, which may lead to loss of agricultural land, displacement of residents and habitat fragmentation. Key strategies to address the social impact include community engagement, responsible land-use planning, environmental impact assessments, and public education.

5.3.3 Public Perception Barriers

Public perception barriers may arise when the public or local communities have limited knowledge of carbon capture technologies and lack trust in the safety of this process and technology. To secure community support and ensure successful project implementation, it is important for the project developers to engage in transparent communication about carbon capture technology with the public. Including the public in decision-making processes, highlighting the environmental benefits, and presenting successful case studies are key strategies for overcoming these barriers and building trust within the community.

6.0 Economic and Funding Considerations

This section focuses on the economic viability of a carbon capture and conversion plant. Many existing facilities in DAF installations, such as power plants, boilers, and generators, can be retrofitted to provide CO_2 sources, and the products (methane and methanol) can be used in these and other DAF facilities that require energy input. Despite the cost variation based on the CO_2 source, H_2 type, technology, and configuration selection, Air Force installations hold promise for carbon capture and conversion. However, a substantial upfront investment is necessary to construct the carbon capture and conversion plant. Fortunately, various federal and state incentives are available to alleviate the financial burden and encourage the deployment of low-carbon technologies.

Techno-economic analysis (TEA) is widely used to assess the economic performance and develop a business model for the deployment of a given carbon capture and conversion technology. Due to the difference in pricing basis, plant size, location, and financial assumptions, the estimated economic performance may vary significantly, even for the same technology. This section delves into existing TEA studies, financial data from news releases, and relevant policies/incentives supporting low-carbon technologies to provide DAF with valuable insights into key cost contributors and production costs of CO_2-derived methane and methanol.

6.1 Estimated Production Cost of CO_2-Derived Fuels

To make informed decisions about the installation of a carbon capture and conversion plant at DAF facilities, decision makers must analyze the cost competitiveness. This section provides insights into the estimated production cost of CO_2-derived methane and methanol based on open-access data.

Methane: The production cost of methane made from CO_2 and H_2, also called synthetic natural gas or SNG, depends heavily on how the hydrogen is made and how efficient the factory is. One study in the U.S. found that making SNG using conventional technology (Figure 2.3) could cost $132 per megawatt-hour (MWh) if hydrogen costs $3 per kilogram and the factory runs 65% of the time (Becker et al. 2019). Another study in Europe found that SNG could cost €150/MWh with the factory running 50% of the time, and €100/MWh if it runs all the time (Schlautmann et al. 2021). To evaluate the economic feasibility, DAF could compare these values with the current market value of fossil-based natural gas, which is $2-9/MMBtu ($7-31/MWh) according to the U.S. Energy Information Administration (EIA 2023). The production cost of CO_2-derived SNG using conventional technology is about 10 times greater. A recent study from Kothandaraman et al. (2021) suggested that the integrated process (as discussed in Section 2.3, Figure 2.6) could make SNG cheaper and more efficient. This could save 32% on the cost of building the factory and 12% on the cost of making SNG. For a cost-effective installation, DAF should consider:

- Low-cost raw materials
- Incentives (carbon credits, as detailed in Section 6.3)
- Emerging technology and process configuration that offer cost benefit via process integration
- New product market other than simply burning SNG as fossil-based fuel (such as considering SNG as a power storage option for renewables).

Methanol: Similar to methane, CO_2-derived methanol has a production cost of twice the market value of fossil-based methanol. A study from the International Renewable Energy Agency suggested a current methanol production cost of $1,600/metric ton if produced from CO_2 (with an assumed price of $50/metric ton) and renewable H_2, with a potential reduction to $600/metric ton with lower renewable power price by 2050 (IRENA 2021). TEA performed on the current state of PNNL's integrated carbon capture and conversion technology (Figure 2.7) suggested a minimum selling price of $4.4/gallon ($1,460/metric ton) for renewable methanol produced from CO_2 captured from a 650-MW natural gas combined cycle plant (Kothandaraman et al. 2022). The sensitivity study suggested that increasing the fluid flow rate through the reactor and methanol selectivity could reduce the selling price of renewable methanol to around $1.4/gal ($470/metric ton). To ensure a return on investment of a carbon capture and conversion to methanol plant, DAF should consider low-cost raw materials, incentives, and alternative process configuration.

6.2 Key Cost Drivers

Regardless the technology selected, costs of CO_2 capture and green H_2 production are the key cost drivers of carbon capture and conversion technologies.

Cost for CO_2 capture: In 2020, the International Energy Agency reported a levelized cost of CO_2 capture of $50-$100 per metric ton CO_2 for power plant application, and a CO_2 pipeline transportation cost of $2-$16 per metric ton CO_2 per 250 km (IEA 2020). The National Energy Technology Laboratory (NETL) reports a carbon capture cost of $46 per metric ton CO_2 for a 650-MW supercritical coal-fired power plant, and $80 per metric ton CO_2 for a 650-MW natural gas combined cycle power plant (James et al. 2019). In NETL's study, Shell's Cansolv, a second-generation aqueous amine solvent, was used for carbon capture, which is a mature technology considered as the benchmark in the U.S. A recent study suggested that water-lean solvents can potentially reduce the cost of carbon capture to below $40 per metric ton CO_2 (Jiang et al. 2023). Considering emerging carbon capture technologies that can lower the cost of CO_2 capture can ultimately reduce the production cost of CO_2-derived methane/methanol and improve the economic feasibility for DAF installation.

Cost of H_2 production: In the U.S., typical production costs of "grey," "blue," and "green" H_2 are $1/kg, $1.4/kg, and $4.4/kg, respectively, assuming a natural gas price of $3.5/MMBtu and a renewable power price of $65/MWh (Robinson 2020). A market equilibrium model developed by the National Renewable Energy Laboratory suggested an H_2 threshold price of $1.7/kg to replace incumbent technologies and accelerate the production of fuels from CO_2 (Ruth et al. 2020). Details about H_2 can be found in the companion emerging technologies review for hydrogen (Briggs et al. 2023). DOE had initiated a program called Hydrogen Shot to accelerate breakthroughs of more abundant, affordable, and reliable clean hydrogen solutions and reduce the cost of clean H_2 to $1 per 1 kg in 1 decade. If successful, this may potentially bring the production cost of CO_2-derived methane and methanol close to that of fossil-based without considering any incentives and credits, and make the technology even more promising for DAF installation.

6.3 Policies and Incentives

There are number of federal-level incentives and policies available in the U.S. to accelerate the development of carbon capture and conversion and renewable fuel production projects, including the following:[1]

- The 45Q tax credit
- Infrastructure Investment and Jobs Act (Bipartisan Infrastructure Law)
- EPA Renewable Fuel Standards
- Blender's tax credits
- Inflation Reduction Act

In addition, 24 states in the U.S. have started adopting specific GHG emission targets to support climate action, while California's Low Carbon Fuel Standard (LCFS) is the first program encouraging the production of renewable fuels to meet GHG emission targets (RFA 2023). Many other states have start adopting LCFS or are considering similar clean fuel programs or standards. It is important for DAF to consider the impact from federal and local policies and incentives to evaluate the economic feasibility of carbon capture and conversion in a given location.

[1] Texts available for 26 U.S. Code § 45Q at www.law.cornell.edu/uscode/text/26/45Q, Infrastructure Investment and Jobs Act at www.congress.gov/117/plaws/publ58/PLAW-117publ58.pdf, EPA Renewable Fuel Standards at www.epa.gov/renewable-fuel-standard-program, Blender's tax credits at www.law.cornell.edu/uscode/text/26/40A, and Inflation Reduction Act at www.congress.gov/bill/117th-congress/house-bill/5376.

7.0 Operational Considerations

There are nearly 30 carbon capture and/or conversion plants in operation worldwide, with another 50+ carbon capture plants in development (Hasan et al. 2022). This section explores operational considerations of carbon capture and conversion systems, including flexible operation for load following and unstable CO_2 sources, utility interconnection, process control, and maintenance.

7.1 Supply/Demand Change Management

Turning CO_2 emitted from DAF facilities into methane and methanol is a promising approach that enables Air Force facilities to move toward carbon-pollution-free energy sources without retrofitting existing facilities. However, these plants often face fluctuating CO_2 supply due to changing energy demand and variable renewable energy availability, as shown in Figure 7.1. This can make it difficult to operate the CO_2 capture and conversion plant efficiently. There are four promising technologies to make carbon capture unit more flexible:

- Exhaust gas venting, allowing the system to bypass a portion of flue gas when production is high
- Solvent/sorbent storage, allowing the system to store excess solvent/sorbent when production is low
- Time-varying solvent regeneration that adjusts the process to match the changing CO_2 supply chain
- Backup utility system, ensuring continuous operation of the plant if its main power source is unavailable.

For the conversion unit, additional points should be considered to smooth fluctuations in the CO_2 supply, including optimal facility sizing and onsite CO_2 storage between peak and down times. In addition, integrated capture and conversion technologies can achieve steady-state operation by controlling the flow of CO_2-rich solvent. These adjustments can make the CO_2 capture and conversion technologies more efficient and effective in reducing GHG emissions.

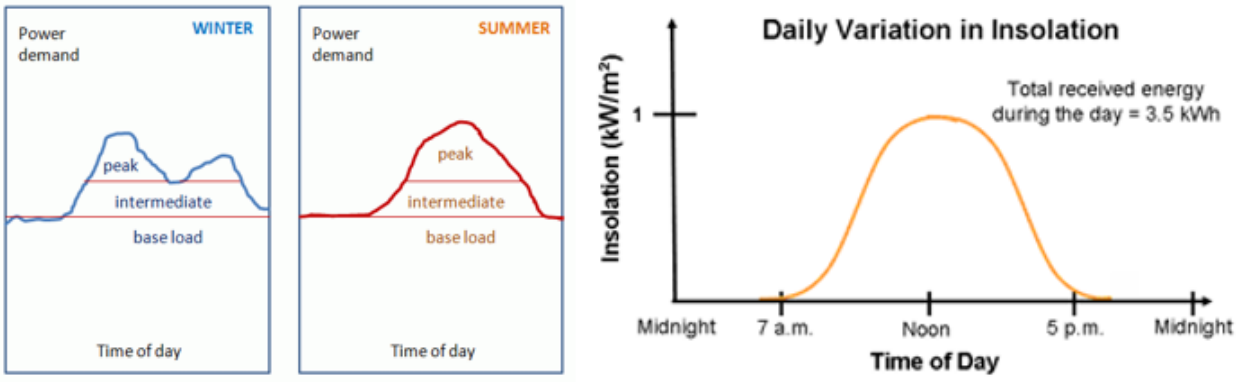

Figure 7.1. Variation in Energy Demand and Generation

7.2 Operations and Maintenance Requirements

Advanced chemicals, materials, and catalysts are used in carbon capture and conversion. For successful operations, it is important to monitor the activity of these materials, conduct regeneration, and/or add fresh material when necessary.

Solvent reclaiming for absorption-based carbon capture: One of the biggest challenges with using solvents to capture CO_2 is that the solvents themselves can break down over time through a process called "solvent degradation." This can be caused by a variety of factors, including the presence of certain trace elements in the CO_2 stream. Amine health and maintainability are critical to operation. To address this issue, a technology called "ion exchange" is often used. The process is called solvent reclaiming, where harmful trace elements in the solvent are removed to keep the solvent functioning properly, extend its lifespan, and ensure continuous operation of the capture plant (Chai et al. 2022).

Solid sorbent replacement and attrition control for adsorption-based carbon capture: Solid sorbent will eventually be physically broken down due to mechanical wear and tear, resulting in attrition. This can be a problem because the tiny pieces can get carried away with the process stream. A baghouse, also known as a fabric filter or dust collector, is frequently used to separate the broken sorbent from process gas stream and control attrition. Of course, even with a baghouse, some sorbent will eventually break down and need to be replaced with fresh material (Sjostrom et al. 2015).

Catalyst activity maintenance for CO_2 conversion: Stability of catalyst activity is crucial for continuous flow operation of a CO_2 conversion facility. Catalyst performance depends on how well the catalyst is maintained during its operational life. One problem with certain catalysts, like copper-zinc oxide (Cu/ZnO), is that the tiny copper particles clump together, which makes them less efficient. Water can also weaken the catalyst's performance. There are three main ways to make the catalysts more durable (Etim et al. 2020):

- Use porous materials to give it more support and prevent the particles from clumping together.
- Use binders (a substance like glue that holds the catalyst particles together and protects them from water damage).
- Use promoted multi-metallic catalyst (catalyst contains multiple metal components and a promoter element that improves the catalyst's selectivity, activity, or stability) (Etim et al. 2020).

It is important to monitor catalyst performance and replace spent catalyst with fresh catalyst when catalyst deactivation is detected.

Water management when using water-lean solvent: Flue gas introduces moisture to the system, while the CO_2 hydrogenation reactions generate water. High water content increases viscosity, making transport within the process difficult. In addition, it may potentially cause catalyst deactivation. To prevent water buildup, water management is critical. Both moisture carried by the flue gas and water generated via reaction need to be removed by dehydration (water removal) technologies.

7.3 Resilience

The following are general recommendations for DAF to consider that can improve the resilience of the carbon capture and conversion plant. During the design phase, the DAF could consider implementing redundant equipment and storage to mitigate single points of failure, installing monitoring systems to detect potential issues, conducting risk assessments, and designing systems to withstand extreme weather events. During operation, it is important to develop robust maintenance plans for all equipment; create emergency response plans for equipment failures; and train operators for safe and effective operation, maintenance, and emergency response procedures. Additional specific consideration should also be given to identifying the most effective resilience strategies, which will vary with the technology selection and plant location.

8.0 Implementation and Siting Considerations

Carbon capture and conversion to methane/methanol technologies can potentially advance an Air Force installation's energy resilience via pursuit of alternative energy sources with low carbon footprint and addressing the growing demands of long-term and large-scale renewable energy and electricity storage. Selecting an appropriate site for a carbon capture plant is crucial for achieving the maximum benefits for the DAF, balancing the cost, demand, logistics, and DAF's broader mission and operational objectives. The following sections outline key considerations for determining the plant location.

8.1 Technology Associated Requirements

Access to CO_2 emission sources: The carbon capture plant uses flue gas as raw material. Thus, a feasible site should have access for the flue gas raw materials. Because the carbon capture cost highly depends on the capture plant capacity and the concentration of CO_2 in the flue gas, a promising site would have a large CO_2 emission source.

Access to utilities: A carbon capture process is energy intensive. A significant amount of steam or electricity (depending on the capture technology) is required to capture CO_2 from flue gas. Therefore, a feasible site should have an onsite utility facility to generate steam and/or access to an electricity grid with stable power supply. The steam demand may be a good application for combined heat and power. If an emerging integrated carbon capture and conversion technology with lower energy demand is considered for implementation, the site should also have access to utilities but with much lower utility demand.

Access to low-carbon H_2 and renewables: H_2 is a key raw material for CO_2 utilization. To build a carbon capture and conversion plant, a feasible site should have access to H_2. However, as discussed in Section 3.1, the use of H_2 from conventional fossil fuels negates the environmental benefits of carbon capture and conversion. To develop a successful business strategy and align with the 2022 Air Force Climate Action Plan (Air Force 2022), it is preferrable to use H_2 derived from renewable resources or plants with low carbon footprint. Therefore, a promising site would have either an onsite renewable H_2 production facility or a long-term agreement with a low-carbon H_2 production plant and transportation infrastructure for stable H_2 supply.

Access to water: Water is used as a raw material for green/renewable H_2 production. If H_2 is produced onsite, the plant would require a significant amount of water. In this case, a feasible site needs to have access to water.

8.2 Land/Space Requirements

The land chosen for a carbon capture plant must meet specific criteria, including sufficient space to accommodate the overall plant footprint (which needs to be evaluated at the front-end engineering design stage), geological stability, suitability for construction, compliance with local regulations, utilities supply, and community support. Ideally, the selected land would allow for scalability, enabling potential expansion to accommodate increased capture capacity or to integrate additional technologies.

8.3 Transportation

The chemicals in a carbon capture and conversion plant, involving flue gas, H_2, and methanol/methane, need to be transported to or from the plant if the plant, resources, and product target market are not co-located. In this case, methanol is a liquid product and is easy to transport, while methane, flue gas, and H_2 are gaseous chemicals, which may lead to high transportation cost. Thus, a feasible site would have easy access to existing transportation infrastructure (i.e., pipelines, liquified gas trucking, compressed gas trucking, etc.). A promising site would have minimum transport distances between the plant, resources, and demanding market.

8.4 Additional Considerations

The following are other factors to consider for prioritizing Air Force installations:

- A location with high natural gas and fuel demands
- Favorable state policy support for renewables and emission reduction
- A site or region with high GHG emissions
- A location that does not pose security risks or compromise sensitive information related to DAF activities
- A site that can support the overall military strategy and enhance operational capabilities.

9.0 Recommendations and Path Forward

Moving forward with the implementation of carbon capture and conversion at Air Force sites, it is recommended that AFCEC conduct a site evaluation, identify the most suitable carbon capture and conversion technologies for the selected site, conduct a feasibility study to address economic considerations, and start from a pilot- or demonstration-scale installation for de-risking and operational resilience. With a successful pilot- or demonstration-scale project, DAF could consider implementing full-scale carbon capture and conversion at suitable Air Force installations.

9.1 Steps to Implement Technology

The following are the main steps for DAF to consider when implementing a carbon capture and conversion plant for DAF application.

Site selection: Identify a suitable location for deploying the carbon capture and conversion infrastructure based on access to resources, end uses, land, and transportation. Section 2.4 details the optimal use cases and scenarios for captured CO_2 in the Air Force facilities.

Technology selection: Once the site is identified, the most suitable technology should be selected based on the DAF's operational requirements, emission characteristics, and scalability. Mature technologies (TRL at or above 8) are available now for all components in the supply chain for CO_2 capture and conversion to methane or methanol. In addition to these mature technologies, there are emerging technologies with TRLs from 3 to 6. These emerging technologies with lower utility consumption and lower capital investment are more attractive from an economic, environmental, and resilience perspective. However, there are risks to directly installing emerging technologies that have not been proven at pilot or demonstration scale at the Air Force facilities. There are several DOE programs aiming to advance the TRL levels of these emerging CO_2 capture and conversion technologies and de-risk and accelerate their demonstration.

Feasibility assessment and financial planning: In tandem with the site and technology selections, a thorough feasibility study must be done to evaluate the technical, economic, and environmental viability of implementing carbon capture technology within the DAF's operational context. Sections 4.0 to 6.0 detail the factors to be considered. In addition, a comprehensive financial plan with budget, funding sources, and potential return on investment should be developed.

Regulatory compliance: The DAF should ensure the carbon capture projects follow local, state, and federal regulations, and obtain necessary permits and approvals to proceed with the implementation.

Engineering design and construction of pilot plant: With a financial plan and permits in place, the DAF can reach out to engineering and design professionals and technology vendors of carbon capture and conversion to develop a detailed engineering design. As mentioned before, pilot-scale testing is highly recommended for the first DAF installation to build internal capacity within the Air Force to manage and operate carbon capture and conversion plants and reduce technology-related risks before a full-scale implementation. With an approved design

created, the DAF can start the construction phase, where all components should be installed and configured correctly.

Monitoring and continuous improvement: During operation, the DAF should use a robust monitoring and reporting system to track plant performance and optimize operating conditions to improve efficiency and resolve challenges and operational issues. In addition, the DAF should establish a framework for continuous improvement, including periodical performance review and system/process update. The experience from the pilot- or demonstration-scale plant can be used for the next DAF installation at a similar or larger scale.

9.2 Recommended Next Steps

In order to construct a pilot- or demonstration-scale carbon capture plant, the DAF could initiate the first three steps outlined in Section 9.1 (site selection, technology selection, and feasibility assessment). These initial steps aim to offer guidelines for the subsequent phases of the project, improving decision-making, resource allocation, and the overall success of the carbon capture initiative. It is important to highlight that during the technology selection steps, the Air Force should pay close attention to the status of ongoing DOE projects aiming to advance and de-risk low-cost emerging technologies. To select a technology and decide when and where to deploy a carbon capture and conversion plant, the DAF should consider all factors associated with operation, technical, regulatory, environment, and economics.

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Appendix A – In-Depth Technology Description

This appendix provides in-depth technology descriptions that support the main conclusions in the report and recommendations for Air Force implementation of a carbon capture and conversion technology.

A.1 Comparison of Different Carbon Capture Approaches

Figure A.1 illustrates three commonly considered approaches for integrating CO_2 capture with conversional power, fuel, and chemical production processes: pre-combustion, post-combustion, and oxy-combustion. The post-combustion strategy, as shown in Figure A.1a, is discussed in Section 2.2.1 for Air Force implementation. The other two strategies and comparison are detailed in this section.

As shown in Figure A.1b, the pre-combustion approach is the most complex, and is widely considered as an intermediate step in processes that generate syngas, such as integrated coal gasification combined cycle (IGCC) plants for power generation and natural gas reforming ($CH_4 + H_2O \rightarrow H_2 + CO$) plants for "blue" hydrogen (a type of hydrogen production that involves the use of fossil fuels, particularly natural gas) production with carbon capture. Using an IGCC plant as an example, fuel is first converted to syngas via gasification ($Coal + O_2 \rightarrow CO + CO_2 + H_2 + CH_4 + H_2O$), then the CO is further converted to H_2 and CO_2 via a water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). CO_2 is removed from the gas mixture (roughly 60-80 mol% H_2 and 20-40 mol% CO_2) via pre-combustion CO_2 capture, and then high-purity H_2 is sent to the combustion unit for power and heat. The combustion creates CO_2-free clean flue gas.

In the oxy-combustion process (Figure A.1c), a boiler fed with pure O_2 instead of air (a mixture of N_2 and O_2) is used for power and heat. The flue gas from the O_2-blow boiler contains mainly CO_2 (over 80 mol%) and H_2O, which can be separated simply via condensation. More difficult gas separation between CO_2 and N_2 is no longer needed (unlike the other strategies). However, a costly air separation unit is required up front to remove N_2 from the air (before it is fed to the boiler) to produce pure O_2.

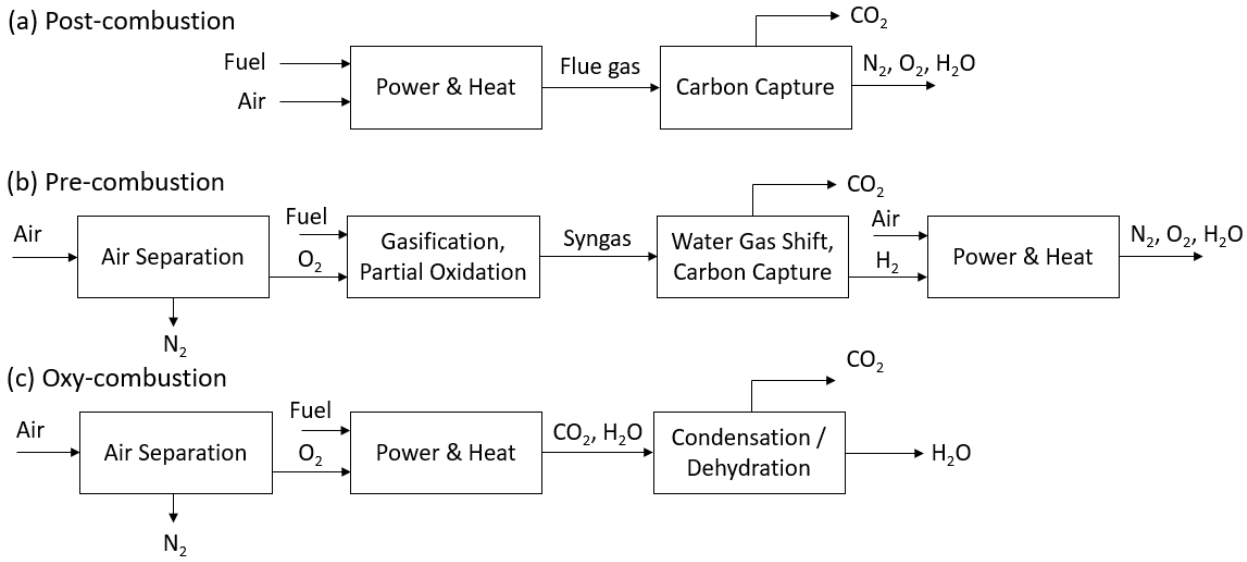

Figure A.1. Approaches and Carbon Capture Points

Table A.1 summarizes the advantages and disadvantages of different CO_2 capture strategies (Dooley 2017; Elhenawy et al. 2020). Among these strategies, post-combustion CO_2 capture has the most mature technologies and requires less retrofitting to existing power and industrial facilities. Therefore, it is more relevant to Department of the Air Force missions from the perspectives of near-term implementation, resilience, and climate control. This appendix focuses on the post-combustion CO_2 capture technologies and their integration with CO_2 conversion technologies for methane and methanol production.

Table A.1. Summary of Post-combustion CO_2 Capture Technologies

Strategies	Advantages	Disadvantages
Pre-combustion (~35% CO_2)	• High CO_2 partial pressure increases the driving force for carbon capture • Lower energy consumption compared to post-combustion • Relatively mature technology • Syngas can be used as fuel or intermediate for chemical production • May increase turbine efficiency	• Operation issues associated with a hydrogen-rich gas • Requires extensive support systems. This complexity leads to high capital and operating cost • Mainly applicable to new plants • Gasification is not widely used in the power and chemical industry
Post-combustion (4-14% CO_2)	• More mature than other strategies • Easily retrofitted to existing plant • Most commonly used CO_2 capture strategy	• Low CO_2 partial pressure at ambient condition leads to lower capture efficiency compared to pre-combustion, which requires large energy consumption for separating CO_2 from the flue gas • Power plant efficiency reductions due to steam consumption
Oxyfuel (85% CO_2)	• Air separation unit is a mature technology • Flue gas contains mainly CO_2 and H_2O, which are easy to separate • Size decrease of boiler and other equipment due to the lower gas volume	• High cost of air separation unit • Retrofitting in existing plant is difficult • Technology needs to be proven for large-scale operations • Potential corrosion issues • High efficiency and energy penalties

A.2 Post-combustion Carbon Capture Technologies

For an amine-based chemical absorption process, the feed flue gas from a coal or natural gas boiler is first sent to a direct contact cooler for sub-cooling and sulfur polishing and a blower to overcome the column pressure drop (James et al. 2019).

In the absorber, the CO_2-lean solvent is fed near the top of the absorber to contact with flue gas in countercurrent flow. CO_2 in the flue gas will be captured by the solvent via chemical reaction. The top section in the absorber is a water wash to mitigate solvent loss in the clean gas stream to the environment. The CO_2-rich solvent from the absorber bottom is pumped to the top of stripper column to separate CO_2 from the solvent, with external heating to generate a high-purity CO_2 stream for the downstream conversion unit and CO_2-lean solvent to be recycled back to the absorber for CO_2 capture. The absorber is operated at low temperature (40-50 °C) while the stripper is operated at relatively high temperature (100-130 °C) depending on the solvents. A

cross heat exchanger is used to exchange heat between the hot lean solvent from the stripper bottom and the cold rich solvent from the absorber column.

The CO_2 absorber is operated at a kinetic limited regime and therefore it is important to ensure sufficient gas/liquid interfacial area for mass transfer. In addition, pressure drop over the absorber needs to be minimized to reduce the capital and energy costs associated with the flue gas blower. Typically, a column filled with structured packing is used for CO_2 absorption. Aqueous amine, such as 30 wt% monoethanolamine (MEA), is considered as a benchmark solvent but is subject to high energy and economic penalties because a considerable amount of water is vaporized and condensed during solvent regeneration (Stowe and Hwang 2017). A number of second-generation aqueous amine solvents, such as piperazine, Shell's Cansolv, and advanced process configurations (Jiang et al. 2021; Van Wagener and Rochelle 2011), have been developed to reduce undesired "water circulation" and associated penalties. Non-aqueous or water-lean solvents are another class of solvents developed recently to minimize water circulation. The non-aqueous solvent developed by RTI International (Lail et al. 2014) and N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA) are two of the leading water-lean solvents and are currently being tested at multiple scales (Swisher 2021).

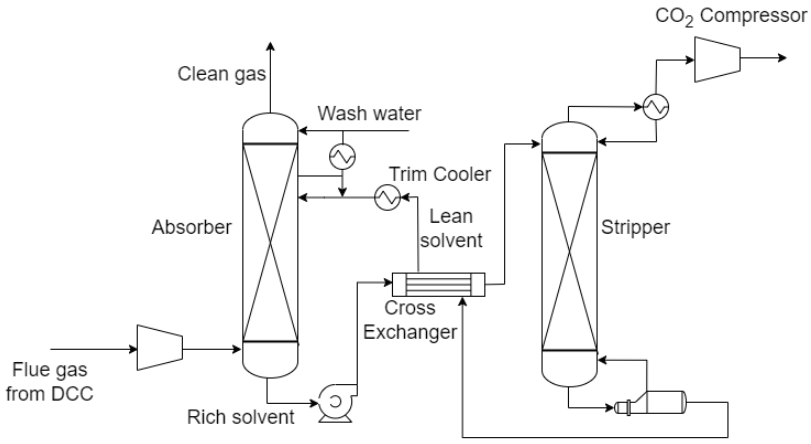

Figure A.2. Process Flow Diagram for Amine-Based Chemical Absorption

Cryogenic separation is a low-temperature physical separation process widely used in industry based on the difference in phase equilibrium (boiling points) and the desublimation properties of components in the gas mixture. Two types of cryogenic methods have been considered for post-combustion CO_2 capture: (1) conventional vapor-liquid (V/L) separation (above -80 °C), which has been used for natural gas purification (Font-Palma et al. 2021); and (2) a nonconventional vapor-solid (V/S) separation (approximately -100 °C).

The V/S cryogenic separation process presented in Figure A.3 is more efficient for post-combustion CO_2 capture than V/L separation because of a much lower operating pressure, near ambient pressure. In this process, the flue gas is first cooled and dried to near ambient temperature, and then slightly pressurized in a blower to overcome the system pressure drop, similar to the absorption process. A direct-contact drying system further reduces the flue gas temperature to -100 °C, at which point CO_2 begins to desublimate to solid, followed by a desublimating heat exchanger to create nucleation sites for desublimating CO_2 particles. The slurry from the desublimating exchanger is pumped to a pressure above the CO_2 triple point and sent to a solid-liquid separator. The solid stream contains mainly CO_2 (80%), which is melted and purified in a distillation column to a purity of greater than 99.9%, pumped, and warmed back

to ambient temperature. A two-stage cascade refrigeration cycle provides chilling for the process.

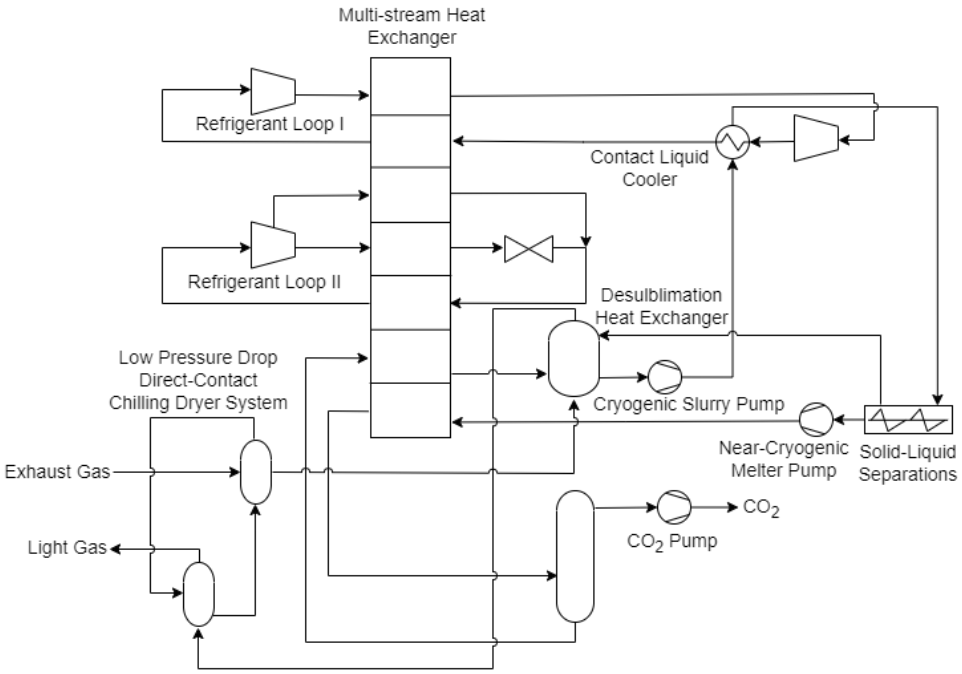

Figure A.3. Process Flow Diagram for Cryogenic Separation

In the membrane process, flue gas is blown to the high-pressure side of the membrane (retentate side). In the membrane modular, CO_2 moves from the retentate side to the permeate side due to the difference in CO_2 partial pressure between two sides, while most of the N_2 stays in the retentate side. CO_2 is separated from flue gas, mainly because of the difference in permeability of components in the gas mixture. The pressure difference between the permeate and retentate sides can be created by compressing the flue gas before feeding to the membrane modular, creating vacuum in the permeate side, and/or using sweeping stream (i.e., steam) in the permeate side to reduce CO_2 concentration and therefore partial pressure. Due to the small CO_2 concentration in flue gas (4-14%) and the limit in separation efficiency, CO_2/N_2 selectivity of membrane technologies, a multi-stage membrane configuration is required to achieve the targeted CO_2 purity (above 95%) and recovery rate (above 90%). Recycling of a portion of permeate and/or retentate products has also been considered for improving CO_2 purity and recovery rate. Similar to the adsorption process, different process configurations can be considered for membrane-based post-combustion CO_2 capture. Figure A.4 illustrates one of the commonly used configurations.

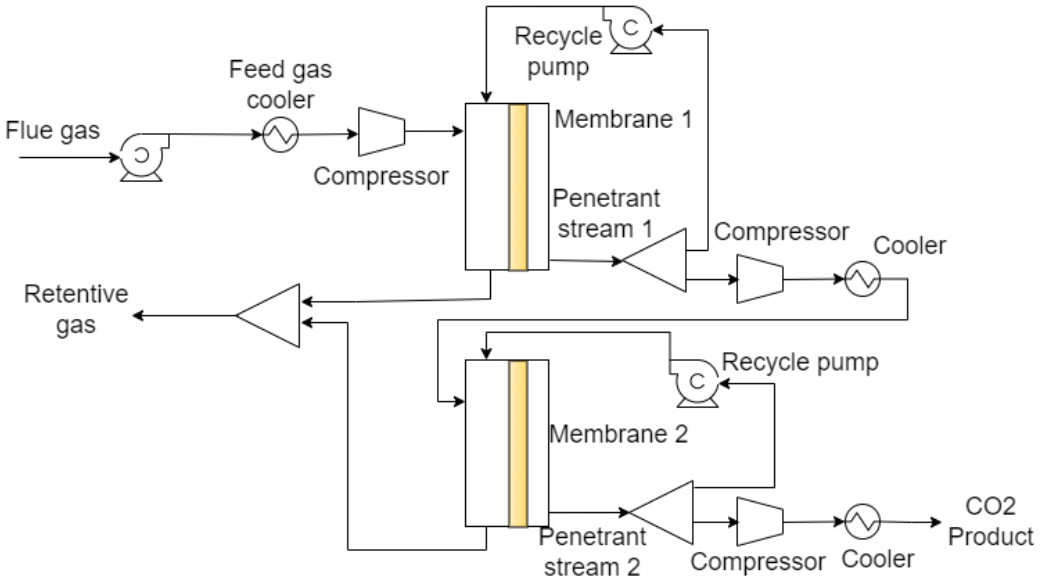

Figure A.4. Process Flow Diagram for Membrane Separation

Most of the commercial adsorption process uses fixed bed design, of which the operation is divided into multiple phases, adsorption and desorption, and intermediate steps in between. In each cycle, flue gas is first blown to the bottom of a bed packed with solid sorbent. In the adsorption phase, CO_2 is adsorbed by the sorbent, while clean flue gas leaves from the top of the packed bed. Then, the sorbent is regenerated by releasing CO_2 in the desorption stage by heating (temperature swing adsorption), reducing pressure (pressure/vacuum swing adsorption), electrical swing adsorption, or their hybrids (Bhattacharyya and Miller 2017). The intermediate phase between absorption and desorption varies with sorbent regeneration approach. As shown in Figure A.5, if temperature swing adsorption is used, one complete cycle will include an adsorption phase, preheating phase, desorption phase, and precooling phase.

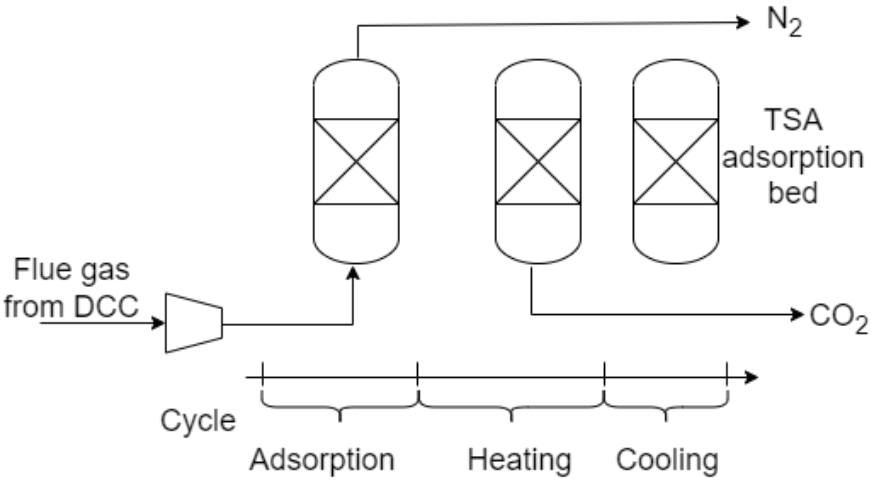

Figure A.5. Process Flow Diagram for Adsorption Separation

A.3 CO_2 Conversion Technologies

Methane: The CO_2 methanation reaction (converting CO_2 into CH_4 by reacting with H_2) enables chemical storage of a significant amount of renewable energy in addition to using large volumes of CO_2. As methanation can yield high conversion of CO_2, the product methane can be easily separated from water and fed into existing natural gas infrastructure. CO_2 hydrogenation to methane ($CO_2 + H_2$ à $CH_4 + H_2O$) is a thermodynamically favorable reaction; however, due to slower reaction rate (kinetics), catalysts are required to improve the reaction rates, selectivity of the desired product, and prevent the production of undesired products.

Several noble (Ru and Rh) and non-noble (Ni and Co) metal-based catalysts have been extensively studied for the selective hydrogenation of CO_2 to methane (also known as the Sabatier reaction) in the temperature range of 250–500 °C and pressures ranging from 1–100 bar. Particularly, Ru-based catalysts show the best activity and stability compared to non-noble metal catalysts (Tan et al. 2022). The common cause of catalyst deactivation is through coke deposition (the accumulation of solid carbonaceous material on the surface of catalysts). Future efforts will likely focus on developing stable and active non-noble metal catalysts with high resistance to carbon deposition. There have also been reports of the electrochemical reduction of CO_2 to methane in addition to thermocatalytic methods (Zheng et al. 2021). There are still challenges, including product selectivity, overpotential,[1] and faradaic efficiency.[2]

Methanol: Many Cu-based metal oxides from the main group and precious-metal-based catalysts have been developed and extensively studied for the hydrogenation of CO_2 to methanol. From a thermodynamic perspective, CO_2 hydrogenation to CH_3OH reaction is favored at lower reaction temperatures, so there is a need to design catalysts that provide high activity at low temperature. Novel reactor design and optimization can also play an important role in improving the activity and selectivity to methanol under mild conditions. The use of membrane reactors (Dang et al. 2019) in place of traditional reactors is an emerging area of research. The byproduct water has a negative effect on the catalyst, resulting in catalyst deactivation by sintering (process in which particles are heated to the point of melting/softening, causing them to bond together and form a denser, more solid mass) (Cui and Kar 2020). Membranes can remove specific products while possibly shifting the equilibrium in favor of product formation. Several issues related to activity and stability of the catalyst, and low methanol yield due to thermodynamic limitations, need to be addressed to encourage widespread industrialization.

There have also been significant advancements in the development of electrocatalysts (a substance that enhances the rate of an electrochemical reaction) for the electrochemical reduction of CO_2 to methanol (Wiranarongkorn et al. 2023; Biswal et al. 2022). High energy is required for the intricate six-electron steps toward methanol formation. There have been many attempts to develop effective electrocatalysts, such as metal alloys, single-atom catalysts, metal-organic framework-based materials, and molecular catalysts, to obtain high methanol selectivity. Designing highly active and stable electrocatalysts that can produce high current densities and good selectivity is crucial due to the tremendous potential for electrochemical CO_2 reduction to methanol.

[1] Overpotential is additional extra voltage required beyond the equilibrium potential for a particular electrochemical reaction to occur at a desired rate.
[2] 100% faradaic efficiency indicates that all the electrical current has been used to drive the desired electrochemical reaction without any side reactions or losses.

A.4 Integrated CO_2 Capture and Conversion

Methane: The economic and energy benefits of an integrated CO_2 capture and conversion process have been recently demonstrated to produce CO_2-neutral synthetic natural gas (SNG) at Pacific Northwest National Laboratory (Kothandaraman et al. 2021). Solid materials with dual functionalities have also been reported for integrated CO_2 capture and conversion. Dual functional materials are non-volatile and less toxic compared to amine-based solvents/sorbents (Omodolor et al. 2020); however, it can be challenging to design dual-functional materials with cooperative CO_2 capture/sorption and conversion. Most of these materials are composed of sorbents (metal oxides and carbonates) and metal catalysts (such as Ru and Ni). In a first step, the sorbent reacts with CO_2 to form bicarbonate ($CO_2 + H_2O + \text{Sorbent} \rightarrow HCO_3^-$ (bicarbonate ions) + sorbent), and in a second step, bicarbonate reacts with hydrogen at high temperature (above 300 °C) to form methane. Some of these materials also require high temperature for capture. Recent studies have also used aqueous sorbents such as aqueous bicarbonate and phosphate solutions to demonstrate integrated CO_2 capture and conversion to methane. Ru- and Ni-based catalysts were used for this approach (Koch et al., 2023). As these materials/systems are at a proof-of-concept stage, the economic viability of practical implementation is unknown.

Methanol: Conventional gas phase methanol synthesis is typically carried out at high pressures and temperatures (more than 200 °C). At this reaction temperature, the exothermic methanol formation reaction ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) competes with the endothermic reverse water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). There has been much interest in low-temperature methanol synthesis from CO_2 hydrogenation to improve the conversion and selectivity. The presence of amines ($-NH_2$) and alcohol (-OH) functionalities in the capture solvent can promote the formation of novel intermediate chemicals such as formamides ($-C(=O)NH_2$) and formate esters ($-C(=O)OCH_3$) (Koch et al. 2023), which are known to favor the formation of methanol at low temperature. Thus, in addition to economic and energy benefits of an integrated CO_2 capture and conversion process, performing the conversion in the capture solvent environment can enhance the methanol synthesis through the formation of novel intermediates.

The feasibility of integrated CO_2 capture and conversion to methanol has also been demonstrated by using EEMPA, an economically viable capture solvent (Kothandaraman et al. 2022). In this process, the amine-based capture solvent will cause catalyst deactivation. Thus, the catalyst must not only be selective in producing methanol but also in preventing the deactivation of the capture solvent during conversion. The study of platinum-based catalyst showed 70% selectivity ($selectivity = \frac{amount\ of\ desired\ product}{amount\ of\ all\ products}$) to methanol at 170 °C with a single pass CO_2 conversion ($single\ pass\ conversion = \frac{amount\ of\ reacted\ reactant}{amount\ of\ initial\ reactant}$) of 29%. The methanol selectivity decreased as the reaction temperature was raised further (to 190 °C); however, there was an excellent (86%) single-pass CO_2 conversion (Kothandaraman et al. 2022). This is the first demonstration of integrated post-combustion CO_2 capture using a single-component, economically viable solvent, and low-temperature thermocatalytic conversion to methanol.

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