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# Sustainable fuel production using renewable energy sources and direct air carbon capture systems

By

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# Abstract

The urgency to mitigate climate change necessitates the transition from fossil fuels to renewable energy sources. Renewable energy obtained from solar, wind and hydropower, plays a crucial role in reducing these greenhouse gas emissions. However, the intermittency of these sources demands active storage solutions. Hydrogen, one of the most versatile energy carriers, presents itself as a promising solution to these climate mitigation challenges. If produced through electrolysis using renewable power, it would be a potentially zero-emission energy carrier. Until enough infrastructure for direct hydrogen utilization is in place, the best use for hydrogen could be through sustainable fuel production. Hydrogen integrated with direct air capture (DAC) technologies to produce sustainable fuels holds a lot of potential, coupled with captured CO<sub>2</sub> for synthetic fuel production like methanol and utilized for synthetic ammonia, offering sustainable alternatives to fossil fuels. These fuels have significant potential to decarbonize various sectors, especially the carbon emission heavy transportation sector. In this thesis, via performing a literature survey, an informative approach to different hydrogen production technologies and DAC technologies is made along with examining synthesis pathways for renewable methanol and ammonia. The technical viability for these technologies is described, as well as the economic viability of these fuels accessed. The potential of those pathways in a Norwegian context is also mentioned. The findings underscore the importance of advancing these technologies to achieve cost competitiveness with fossil fuels.

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# Abbreviations

AEA	Ammonia Energy Association
ATR	Autothermal reforming
AWE	Alkaline water electrolysis
CAES	Compressed air energy storage
CAPEX	Capital expenditures
CCS	Carbon capture and storage
DAC	Direct air capture
ESA	Electro swing adsorption
ESS	Energy storage systems
kJ	kilo Joule
GHG	Greenhouse gas
Gt	Giga tonne
GW	Giga watts
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
Mt	million metric tonnes
OPEX	Operational expenditures
PEM	Proton exchange membrane
PHS	Pumped hydroelectric storage
POX	Partial oxidation
PSA	Pressure swing adsorption
PV	Photovoltaic Panels
RES	Renewable energy source
RWGS	Reverse water gas shift
SMR	Steam methane reforming
SOEC	Solid oxide electrolysis cells
TRL	Technology readiness level
TSA	Temperature swing adsorption
WGS	Water gas shift

# 1. Introduction

The immediate need to mitigate climate change necessitates a rather rapid transition from fossil fuels to renewable energy sources. The continued use of fossil fuels is a major contributor to greenhouse gas emissions, which drive climate change and its associated impacts on the environment, human health, and the global economy. Renewable energy, derived from solar, wind and hydropower, offers a sustainable solution to reduce these emissions. However, the intermittent nature of these sources presents a significant challenge, requiring effective storage solutions to ensure a stable and reliable energy supply.

Hydrogen, as one of the most versatile energy carriers, presents itself as a promising solution to these climate mitigation challenges. Despite its advantages, the widespread adoption of hydrogen is currently hindered by the lack of infrastructure for its direct utilization. Therefore, the best interim use for hydrogen could be through the production of sustainable fuels.

Combining hydrogen with carbon dioxide (CO<sub>2</sub>), captured from the atmosphere using the cutting-edge carbon capture technology, DAC, enables the production of synthetic fuels. One of these fuels, methanol offers sustainable alternatives to fossil fuels, and have significant potential to decarbonize various sectors, particularly sectors of low potential for electrifying. Ammonia, one of the biggest carbon emitters in the chemical industry is another fuel pathway evaluated from hydrogen utilization. The pairing of renewable hydrogen with DAC technologies for fuel production, not only provides a pathway for reducing greenhouse gas emissions (GHG), but also enhances energy security and supports the transition to a low-carbon-economy.

#### **1.1. Background information**

#### 1.1.1. Climate change

The effect of human activities on global warming through emissions of greenhouse gasses (GHG) raises an urgent call for a shift in our energy supply and consumption patterns. According to the "Climate Change 2023 Synthesis Report" by Intergovernmental Panel on Climate Change (IPCC), the period from 2011 to 2020 saw global temperature increases of 1,1°C above pre-industrial levels (1850-1900). It is a direct result of increasing GHG emissions primarily from unsustainable energy production and consumption (IPCC, 2023).

This warming has led to widespread and rapid changes across the planet, adversely affecting weather patterns, oceans, ice caps and ecosystems. The continuation of increasing GHG emissions will only escalate this global warming. with projections from the IPCC indicating a potential for surpassing 1,5°C in the near term, thereby intensifying various climate hazards including floods, droughts, hurricanes, heatwaves, severe storms, and landslides. Rapid and sustained reductions in emissions could noticeably slow the global warming within a couple of decades. However, current progress in adaption and mitigation is insufficient to meet these needs, with significant gaps between policy aspirations and the reality of implementation of emission reduction measures. Extraction and use of fossil fuels such as coal, oil, and gas (e.g., for energy sector) has been the main contributor to the climate challenges. With the climatically destructive reliance on fossil fuels accounting for over 75% of global GHG emissions and nearly 90 % of CO<sub>2</sub> emissions (United Nations), there is a critical need for immediate action to limit emissions and transition to renewable energy sources (RES). The most prominent sources of renewable are being solar, wind and hydropower. This transition involves not only adopting renewable energy at a much faster pace but also integrating climate actions into broader sustainable development goals, promoting equity and international cooperation as key enablers for change (IPCC, 2023).

#### 1.1.2. Renewable energy sources

Renewable energy sources are derived from natural processes that replenish at a rate faster than they are consumed, allowing for sustainable usage with minimal emissions of air pollutants and greenhouse gasses (GHG). The primary sources of renewable energy, solar, wind and hydropower, each offer sustainable power solutions with unique advantages and challenges.

Solar energy, the most abundant renewable resource, harnesses sunlight to generate electricity and heat. Modern solar technologies, such as photovoltaic panels (PV) and concentrated solar power systems are effective even under varied sunlight conditions. The Earth receives approximately 10000 times more solar energy daily, than the total global energy consumption(United Nations), highlighting the potential of solar power to meet the global energy needs. Over the last decade, reductions in manufacturing costs have made solar electricity more economically viable, facilitating widespread adoption of solar installations globally (United Nations).

Wind energy harnesses the kinetic energy of air movement, captured by turbines placed both onshore and offshore. Wind turbine technology designs continues to evolve, aiming to maximize energy capture across different wind conditions and minimize production costs. Wind energy is capable of potentially surpassing global electricity demands, making it particularly attractive for high speed wind areas, including remote and offshore locations, where consistent wind conditions allow substantial electricity generation (Ellabban et al., 2014; United Nations).

Hydropower, the most established among renewable resources, generates power from the energy of moving water, from higher to lower elevations. This mechanical energy is converted to electrical energy in large-scale reservoir hydropower plants and river systems that utilize natural river flows. Hydropower facilities often also provide multiple community benefits, including drinking water and flood control. With one of the highest energy conversion efficiencies, hydropower remains a proven and reliable energy source, based on more than a century of experience. Although primarily associated with dams, emerging technologies are expanding its scope to include wave and tidal power (Ellabban et al., 2014; United Nations).

Primary advantages for solar energy include the potential infinite energy supply and lack of pollution during operation. However, the intermittent nature of sunlight requires effective storage solutions, and initial cost, through decreasing, are still significant. For wind energy, an abundant energy source with minimal environmental impact and relatively low construction costs, is offered. Its main drawbacks include dependency on wind availability and potential visual and special impacts on landscapes. Advantages of hydropower include the capability of providing power on-demand, unlike solar and wind. It also supports recreational opportunities such as fishing and boating. On the other hand, it can have significant ecological impacts, and potential dam failures pose risks to surrounding communities and ecosystems. Additionally there is a challenge for new projects, with most optimal dam cites largely (Ellabban et al., 2014).

#### **1.1.3.** CO<sub>2</sub> capture and storage

 $CO_2$  capture and storage (CCS) is a combination of technologies designed to mitigate the impact of greenhouse gasses in the atmosphere by capturing  $CO_2$  directly from emission sources, transporting it, and securely storing it away from the atmosphere. As outlined by Metz and colleagues in the IPCC's special report on carbon dioxide capture and storage, the principal sources of  $CO_2$  emissions include large combustion units in power generation and smaller sources like vehicles, building furnaces, as well as industrial processes and deforestation (Metz et al., 2005). Addressing these emissions through CCS could significantly lower the greenhouse gas footprints of these activities.

The CCS process involves three main steps, capture, transport, and storage. CO2 capture technologies are divided into three main categories, pre-combustion, post-combustion and oxyfuel combustion. Pre-combustion capture involves converting fossil fuels into a gaseous mixture of hydrogen and CO<sub>2</sub>, before separating out the CO<sub>2</sub>. This method is most suitable for processes using natural gas or syngas (Sanz-Pérez et al., 2016). Post-combustion capture, applicable to existing power plants, involves capturing CO<sub>2</sub> from flue gasses after combustion. This method can be widely implemented in power plants and industrial processes that burn fossil fuels (Metz et al., 2005). Oxyfuel combustion, still in its early stages, uses pure oxygen instead of air for combustion resulting in highly CO<sub>2</sub> concentrated exhaust gasses, simplifying the capture process (Fawzy et al., 2020). Once captured, the CO<sub>2</sub> must be transported to storage sites. This storage involves injecting the CO<sub>2</sub> into geological formations or deep ocean reservoirs, where it is trapped for millennia, thus removing it from the atmosphere. This vital step ensures the long-term effectiveness of CCS, as the integrity of the storage site determines the potential for leakage and overall success of process. The captured CO<sub>2</sub> can also be stored by usage in industrial processes to create sustainable fuels. Transportation is primarily done via pipelines or ships, depending on the quantity of CO<sub>2</sub> and distance to storage site (Fawzy et al., 2020; Metz et al., 2005).

#### 1.1.4. Direct air capture for removing CO<sub>2</sub> from the atmosphere

There is still a long way to go for the infrastructure to support CCS on a global scale. In addition, the implementation of CCS technologies needs frameworks that govern the processes, as well as monitoring of the emissions. These regulations are needed to ensure the environmental integrity, the operational safety and liability in case of leakage and other unforeseen issues (Fawzy et al., 2020). Public perception also plays a pivotal role, as community acceptance is essential for development of projects and infrastructure. Transparent communication, engagement and addressing environmental concerns will be key for gaining public trust.

Direct air capture (DAC), a concept first introduced by Lackner and colleagues in 1999 (Lackner et al., 1999) and defined as "the direct extraction of CO<sub>2</sub> from ambient air" (Sanz-Pérez et al., 2016). This technology could play an important part of meeting net-zero goals.

Unlike CCS methods that are tied to point emission sources, DAC can be deployed virtually anywhere at any time, providing major flexibility in terms of location. DAC's primary feedstock is ambient air, which is abundantly available. This means that the potential for DAC to capture not only new emissions but also already existing emissions (legacy emissions). According to the "Direct Air Capture" report from the International Energy Agency (IEA) from 2022, DAC could be crucial for achieving net zero emission by mid-century (2050) (IEA, 2022). As of 2022, there was 18 operational DAC facilities worldwide, all small scale in total capturing nearly 10 kt (kilotons) of CO<sub>2</sub> annually. Also, significant investments and policy support illustrate the growing momentum behind this technology, meaning that the amount CO<sub>2</sub> captured directly from air will increase drastically in the future. Among such supports are the commitment of 3,5 billion dollars in the USA to establish four DAC hubs as well as additional funding for DAC research and development in countries like the United Kingdom, Canada, and Australia. The first large scale DAC plant projected to catch 0,5 Mt (million metric tons) CO<sub>2</sub> per year, is currently being built in the USA called the STRATOS, made by 1PointFive and is expected to become operational by 2025 (1PointFive, 2023; IEA, 2022). The IEA's net zero scenario presents a rapid scale up of DAC, forecasting that DAC will capture around 85 Mt CO<sub>2</sub> in 2030 and 980 Mt CO<sub>2</sub> in 2050, which requires a massive scale up from today.

#### 1.1.5. Intermittency and the need for storage

With the global attention shifting towards innovative renewable energy sources, like solar and wind power. Addressing their inherent intermittency becomes important for maintaining a stable and reliable energy supply. Unlike traditional sources RES depend heavily on environmental conditions, leading to fluctuating outputs based on weather variations and time of day. This variability can result in periods of both energy surplus and energy deficit. This challenge for electric grid stability and reliability, necessitates the development of effective energy storage systems (ESS) that can bridge the gap between energy supply and demand at different timescales. ESS are essential for storing the surplus energy produced during peak conditions, allowing it to be used during periods of low energy production. This capability not only helps in stabilizing the electric grid, but also in ensuring a continuous energy supply, thereby enhancing the efficiency of the power network. Without these systems, energy produced by renewable energy sources could not be stockpiled resulting in potential energy loss and economic inefficiencies (Suberu et al., 2014). Energy storage technologies vary from short-term, medium-term, and long-term storage. For short-term energy storage, technologies that manage energy fluctuations ranging from seconds to minutes are ideal. These systems can quickly release energy, such as batteries and flywheels. For medium-term energy storage, battery systems such as lithium-ion and lead-acid are widely used for addressing energy intermittency of a scale from minutes to hours. These systems are crucial for daily load leveling, where energy generated during periods of high output (e.g., midday solar peak) is stored and then used during periods of low production (e.g., nighttime). For long-term energy storage mechanical systems like pumped hydroelectric storage (PHS) and compressed air energy storage (CAES) are used in scales from hours to days to even seasons. These storage options allow for the storage of large quantities of energy that can be utilized to overcome prolonged periods of low energy generation (Ibrahim et al., 2008; Mitali et al., 2022; Suberu et al., 2014).

Hydrogen also represents a viable option for energy storage, suitable for both medium and long-term applications. This adoption comes with its challenges, for instance, to utilize hydrogen as a transportation fuel, it must be compressed to high pressures, or be liquified, which involves cooling it to extremely low temperatures, due to hydrogen's low energy density in gaseous form (Mitali et al., 2022; Nikolaidis & Poullikkas, 2017). Furthermore, the current infrastructure for hydrogen transmission is not widespread. According to Hassan and colleagues (2023), some hydrogen pipelines and storage facilities currently exists, typically concentrated in specific regions, not interconnected on a global scale. This limitation in infrastructure restricts the scalability of hydrogen systems and constrain its distribution (Hassan et al., 2023).

Until enough infrastructure is in place, hydrogen utilization for fuel production could be a possible solution. As highlighted by the IEA in their Future of Hydrogen report (2019), hydrogen shares many similarities with electricity in that it can be sourced from various energy sources and technologies and used in a wide range of applications. Its role as a chemical energy carrier is strong due to its ability to be stored and transported, much like conventional fossil fuels. This capability makes hydrogen attractive for sectors where direct electrification is challenging, such as part of transportation, heavy industry, and the aviation sector (IEA, 2019). Especially the utilization of hydrogen for synthetic fuel production.

#### 1.1.6. Fuel production via stored hydrogen and captured CO<sub>2</sub>

Among synthetic fuels, methanol (CH<sub>3</sub>OH) and ammonia (NH<sub>3</sub>) stand out due to their potential to be synthesized in environmentally sustainable ways. Methanol can be produced

via direct hydrogenation of captured CO<sub>2</sub>, ideally using green hydrogen generated from electrolysis using renewable electricity and DAC for CO<sub>2</sub>. This process not only produces a versatile chemical feedstock and fuel, but also ensures that the methanol generated is largely carbon-neutral (IRENA & METHANOL INSTITUTE, 2021).

Similarly, ammonia production, traditionally reliant on hydrogen from natural gas, can transition to a greener pathway using renewable hydrogen. When combined with atmospheric nitrogen, the process yields ammonia without the carbon emissions associated with conventional methods. This green ammonia can be utilized as a direct fuel or as chemical fertilizer.

Both methanol and ammonia can be seamlessly integrated into existing infrastructure, offering a method to decarbonize sectors heavy reliant on fossil fuels. By the focus on these two chemicals, hydrogen use will be enabled. Having an immediate impact on reducing carbon emissions, while the broader infrastructure is being developed. (IEA, 2019; Zang et al., 2021).

#### 1.1.7. Target fuels – Current status and description

**Methanol** is a key feedstock in the chemical industry, used to produce various other chemicals like ascetic acid and for base material in acrylic plastic. According to "Innovation Outlook: Renewable Methanol" (2021) report by the International Renewable Energy Agency (IRENA) in partnership with Methanol Institute (MI), 98 Mt methanol are produced annually, predominantly from natural gas. The life-cycle emissions from methanol production are significant, contributing approximately 0.3 Gt (gigatons) CO<sub>2</sub> annually, which accounts for about 10 % of the total emissions from chemical sector (IRENA & METHANOL INSTITUTE, 2021). The report also highlights the doubling of methanol produced over the last decade, with substantial growth in China. Looking forward, production is projected to rise to 500 MtCH<sub>3</sub>OH/ year by 2050, potentially releasing 1.5 Gt CO<sub>2</sub> annually, if still reliant on fossil fuels (IRENA & METHANOL INSTITUTE, 2021).

Ammonia is the second most produced chemical by mass globally, and is essential for producing nitrogen fertilizers, that support food production for approximately half of the global population. Traditionally, most ammonia is synthesized from natural gas (72 %) and coal (22 %), contributing around 0.5 Gt of CO<sub>2</sub> emissions annually, which represents 1 % of global CO<sub>2</sub> emissions and 15 – 20 % of chemical sector emissions (IRENA & AEA, 2022). As the comprehensive "Innovation Outlook: Renewable Ammonia" (2022) report published by

IRENA and the Ammonia Energy Association (AEA), the global production from ammonia was 183 Mt in 2020, with projections showing increase to 223 Mt by 2030, largely driven by population growth and corresponding demand for fertilizer (IRENA & AEA, 2022).

# 1.2. Methodology

To conduct this thesis, a comprehensive literature review was carried out on different topics including climate targets and the need for renewable energy sources, DAC technologies, hydrogen production technologies, and fuel synthesis of methanol and ammonia. The following subsections outlines the research methods, criteria used to gather and select the relevant literature, as well as reference management.

#### 1.2.1. Search engines and databases

To access a wide array of scholarly articles and reports, a combination of search engines and databases was utilized. Google Scholar, although very broad in scope, was invaluable for identifying highly cited research. Oria, a robust database, was particularly valuable for the ability to filter results to only peer-reviewed articles, ensuring the scholarly integrity of sources accessed. It was also valuable for its access granting abilities, via UiS institution access to multiple articles otherwise restricted. Science Direct offered a search engine to a comprehensive bibliographic database of scientific publications from Elsevier, essential for acquiring in depth technical and scientific knowledge.

#### **1.2.2.** Use of web sources

In addition to academic search engines and databases, several web sources for up-to-date information and specific data, was consulted. Vital insights were gained from reports by established organizations and their webpages. Including information about climate change and renewable energy from the United Nations, the "AR6 Synthesis Report" from the IPCC on climate change, multiple reports from the IEA, concerning, direct air capture, global hydrogen review and the future of hydrogen. Along with 2 very comprehensive reports from IRENA (with MI and AEA respectively) considering renewable methanol and ammonia.

#### **1.2.3.** Search terms

This review employed strategic searches to systematically explore and gather literature relevant to each topic addressed. For instance, for climate change and renewable energy, searching included terms such as "climate change mitigation", "renewable energy adoption", "greenhouse effect", and "renewable energy sources". For DAC technologies, search terms

such as "direct air capture", "CO<sub>2</sub> separation", "CO<sub>2</sub> storage", "liquid absorption" and "solid adsorption" were included. For hydrogen production technologies, searches such as "hydrogen production", "steam methane reforming", "water electrolysis" and "renewable hydrogen" were used. For fuel synthesis, searches included key terms like "fuel synthesis", "methanol synthesis from CO<sub>2</sub>", "Haber-Bosch synthesis", "ammonia synthesis", "renewable methanol" and "renewable ammonia". For the technological integration and system analysis terms like "DAC and CO<sub>2</sub> utilization" and "system integration of renewable energy", were included.

#### 1.2.4. Criteria for inclusion and exclusion

The selection of literature was based on relevance to the thesis topics, structural and linguistic quality of publications, and their ability to provide a thorough understanding of the subject matter. Relatively high citation counts on Google Scholar, as well as peer-reviewed articles from Oria, were criterions. Thereby reflecting the research impact and recognition within the scientific community. Additionally, reports from organizations and agencies were crucial for this study. Exclusions occurred from sources of declining content quality or simply not being within the scope of this thesis.

#### 1.2.5. Reference management

For reference management the reference tool EndNote was used. Its integration with Google Scholar facilitated the direct import of citations, although manual entry of DOI and URL were required to ensure the completeness of bibliographic data, and its citation format was checked to ensure correct citation style. This tool was very helpful in maintaining an organized and reliable reference system throughout the thesis.

#### **1.3.** Scope of the thesis

This thesis aims to explore synthetic fuel production through the integration of hydrogen from renewable electricity both with direct air capture technologies and without. The scope of this research is defined by following parameters.

The study focuses on solar, wind and hydropower as primary sources of renewable electrical energy, assessing their role and potential in reducing reliance on fossil fuels. It examines current DAC technologies, specifically absorption-based Liquid-DAC (L-DAC) and adsorption-based Solid-DAC (S-DAC), providing an informal review of their operational efficiencies, challenges, and potential for scaling. For hydrogen production technologies, for

renewable, only water electrolysis (including alkaline water electrolysis (AWE), proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC)) are considered. Additionally non-renewable methods (steam methane reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR)) are reviewed. For fuel synthesis, the synthetic production pathway of renewable methanol and ammonia is provided. Methanol from green hydrogen integrated with DAC. And ammonia from green hydrogen, with nitrogen. Focusing on the feasibility and sustainability of these processes. As for mathematical models and simulations, that have significant importance for a detailed technical analysis, they were not included in the scope of this thesis to keep the focus on technological review and broad spectra informality. The technologies are mainly evaluated in a global context, with somewhat local contexts also mentioned, considering applicability and scalability.

#### **1.4.** Thesis structure

The thesis is structured into several chapters, each designed to explore different aspects of sustainable fuel production, providing a comprehensive understanding of the subject.

Chapter 1 provides an overview of the thesis, including the background information covering climate change, highlighting the urgency of transitioning to renewable energy sources, the specific renewable resources considered, the concept of CCS, the potential of DAC, the intermittency of renewable resources, storage options, the potential for fuel synthesis from CO<sub>2</sub> integrated with H<sub>2</sub> for methanol synthesis, ammonia synthesis from H<sub>2</sub> and mentioning current status of chosen fuels. Thereby setting the stage for the necessity of the different technologies described in thesis and outlining methodology of study and scope of thesis.

Chapter 2 presents a detailed review of currently used DAC technologies, focusing on liquid absorption and solid adsorption process systems, as well as briefly review emerging technology. This chapter assesses the operational mechanisms, efficiency, challenges, and prospects of these technologies.

Chapter 3 discusses hydrogen production methods from non-renewable production and renewable hydrogen production using water electrolysis. This chapter evaluates the technologies based on their efficiency and advantages, highlighting suitability for integration with DAC and for sustainable fuel production.

Chapter 4 explores the synthesis of renewable methanol and renewable ammonia respectively, methanol synthesized from renewable hydrogen integrated with captured CO<sub>2</sub>, and ammonia synthesized from renewable hydrogen without. It details pathways, cost comparisons and potentials for renewable methanol and renewable ammonia production.

Chapter 5 summarizes the findings of the thesis, discussing the potential of chosen fuel synthesis pathways. This chapter also highlights necessary future research directions and the potential economic and environmental impacts of deploying these technologies.

# 2. Overview of direct air CO<sub>2</sub> capture technologies

Separation of CO<sub>2</sub> from atmospheric air differs significantly from point sources (e.g., power plants). In the latter case, flue gas streams contain relatively higher CO<sub>2</sub> content (4-12vol.%) than air with CO<sub>2</sub> concentration of approximately 0,04vol% (Erans et al., 2022). This means that any DAC separation process will have a higher thermodynamic challenge and be less favorable for producing the same CO<sub>2</sub> output from air as compared to concentrated sources like flue gas. This gives an increasing energy input required to separate and concentrate the CO<sub>2</sub>. According to Erans and colleagues (2022), the production of CO<sub>2</sub> captured from air instead of flue gas, would increase the minimum energy requirement at a factor of 3.7, compared to traditional CO<sub>2</sub> capture from flue gas. They further highlight that estimates up to 10 GJ per tCO<sub>2</sub> has been made for DAC, while capture from point sources currently requires 2-4 GJ per tCO<sub>2</sub>. Thereby acknowledging that no DAC process would be energetically or economically competitive with capture from concentrated sources under similar capture conditions (Erans et al., 2022).

This fundamental difference and dilution challenge, underscores the need for growing interest in direct air capture (DAC) technologies, necessitating innovative solutions to these challenges, driven by urgent global need to achieve net-zero emissions. The IEA "Direct Air Capture 2022" report provides a comprehensive analysis, emphasizing the role of DAC in global reduction strategies, its technologies and cost estimates. Erans et al (2022) dives into the technological and economic sides of DAC, discussing the efficiency and challenges of various sorbent- based technologies. Similarly, Sodiq et al (2023) explore the advancements in sorbent systems, including both liquid and solid options. Keith and colleagues work,

presents a detailed liquid DAC process in an industrial plant, with their industrial design reflecting real development from company Carbon Engineering (Erans et al., 2022; IEA, 2022; Keith et al., 2018; Sodiq et al., 2023).

# 2.1. Principle of DAC

DAC primarily relies on the sorption phase, where specialized sorbent materials or liquid chemical agents selectively bind with CO<sub>2</sub> molecules from ambient air. This selectivity is important, allowing other gasses (nitrogen and oxygen) to pass through unaffected. Sorbents typically involve hydroxide or amine-based chemistry cycled efficiently between ad/absorption where CO<sub>2</sub> is captured and desorption where its released, allowing sorbent regeneration phase. These cycles demand that sorbents maintain high selectivity, robust capacity, and fast kinetics to be practically viable. Furthermore, the sustainability of these processes is crucial in that sorbents must exhibit thermal and chemical stability and mechanical integrity (for solid adsorbents). If DAC systems operates on fossil fuel-based energy, the overall benefit of the captured CO<sub>2</sub> could be negated by the emissions from these energy sources, therefore, integrating DAC with renewable energy sources is key to ensure the process remaining carbon-negative. This integration both helps in reducing the carbon footprint of DAC, but also promoting use of renewable energy (Erans et al., 2022; IEA, 2022; Sodiq et al., 2023).

#### 2.2. DAC technologies

The technological approaches to DAC can be broadly classified into two categories, high temperature liquid DAC (L-DAC) and low temperature solid DAC (S-DAC), each with different mechanisms and operational settings (IEA, 2022; Keith et al., 2018).

#### 2.2.1. L-DAC systems

L-DAC systems use a liquid solvent-based capture process to capture  $CO_2$  from the atmosphere. The air contractor is the initial unit where the ambient air comes into contact with the  $CO_2$  absorbing liquid solvent (for example calcium hydroxide,  $Ca(OH)_2$ ). This is usually a large unit with fans that pull air through the system, where the design ensures maximum contact between air and solvent. The chemical reaction for the  $CO_2$  absorption is shown in Equation 1, where calcium carbonate ( $CaCO_3$ ) is formed. The formed  $CaCO_3$  is then processed into compact  $CaCO_3$  pellets for easier handling in the pellet reactor. Further the calcium carbonate, for separation is dried and undergoes calcination at temperatures above

700 °C in the calciner unit, to form calcium oxide. Thereby releasing a concentrated stream of CO<sub>2</sub>, shown in Equation 2. Lastly the calcium hydroxide undergo regeneration in the slaker unit via hydration of calcium oxide shown in Equation 3 (Erans et al., 2022; Sanz-Pérez et al., 2016). Visual representation of process is shown in Figure 1.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$
 (CO<sub>2</sub> absorption, air contractor) (Equation 1)  
 $CaCO_3 \rightarrow CaO + CO_2$  (CO<sub>2</sub> release reaction, calciner) (Equation 2)  
 $CaO + H_2O \rightarrow Ca(OH)_2$  (Calsium oxide hydration, slaker) (Equation 3)



Figure 1: L-DAC based on high temperature liquid sorbent by Carbon Engineering. Obtained from (Carbon Engineering, 2024)

## 2.2.2. S-DAC systems

The S-DAC systems utilize solid adsorbents operating through an adsorption-desorption cycling process. The adsorption takes place at ambient temperature and pressure, where air is drawn into the collector unit and CO<sub>2</sub> is captured by a sorbent material filter and released through controlled heating and depressurization in a temperature-swing adsorption (TSA). It works in a way that when the sorbent material filter is fully saturated, the collector is closed and heated (up to 80-100 °C), with a vacuum simultaneously being applied. This facilitates the release of the captured CO<sub>2</sub> simultaneously regenerating the sorbent filter (IEA, 2022). One S-DAC unit has a capture capacity of 50 tCO<sub>2</sub> per year, and can also extract water from the atmosphere, given that local conditions allow, with the early prototypes being able to remove 1 tonne of water per tonne CO<sub>2</sub> (IEA, 2022). A S-DAC plant has modular design, which means as many units as needed can be included, this is important due to the need of multiple units simultaneously in capture and regeneration stages for larger implementation. Visual representation shown in Figure 2. The largest operating S-DAC plant currently is

Climeworks's "Orca" with a capture capacity of  $4000 \text{ tCO}_2$  per year (IEA,2022), all through that will change soon with "Mammooth" from Climeworks launching in May 2024, with a capture capacity up to  $36000 \text{ tCO}_2$  including 60 collectors (Climeworks, 2024).



Figure 2: S-DAC based on low temperature solid adsorbent process inspired by Climeworks "Orca" plant. Obtained from (IEA, 2022)

## 2.2.3. Comparison L-DAC & S-DAC

Both L-DAC and S-DAC his distinct operational characteristics, energy requirements, and potential environmental impacts making them suitable for different applications. Based on data from the extensive "Direct air capture 2022" report from IEA, Table 1 summarizes key features of these two technical approaches.

Feature	L-DAC	S-DAC	
CO <sub>2</sub> separation	Liquid sorbent	Solid adsorbent	
Heat consumption	5.5-8.8%	7.2-9.5%	
Specific energy consumption (GJ/tCO <sub>2</sub> )	80-100%	75-80%	
Electricity consumption	0-20%	20-25%	
<b>Regeneration</b> temperature	900°C	80-100°C	
Regenaration pressure	Ambient	Vacuum	
Capture capacity	0.5 MtCO <sub>2</sub> /year	50 tCO <sub>2</sub> /per unit anually	
Approximate levelized cost of capture (USD/tCO <sub>2</sub> )	Up to 340 USD	Up to 540 USD	

Table 1: Key features of L-DAC & S-DAC. Adapted from (IEA, 2022).

#### 2.2.4. Emerging DAC technology

Whilst DAC based on sorbent processes are now relatively well established, there are several emerging technological processes at earlier stages, that could have the ability to make an impact. One emerging DAC technology is electro-swing adsorption (ESA).

ESA operates on an electrochemical principle where CO<sub>2</sub> is adsorbed onto a solid electrode at negative charge and then released at reversed charge. This allows for the capture of CO<sub>2</sub> from both highly concentrated and dilute sources without the need for high temperatures or pressures, making ESA energy efficient and potentially less costly (Erans et al., 2022; IEA, 2022). Without the need for equipment to maintain pressure or temperature, the advantage of ESA would include high efficiency, reduced operational complexities and scalability (Voskian & Hatton, 2019). However, the main disadvantage to consider, is that the current technology readiness level (TRL) of ESA is low, indicating the requirement for substantial development before commercialization. The main problem being that ESA yet cannot adsorb CO<sub>2</sub> from sources as dilute as ambient air (0,04%), with lowest dilution adsorption currently being ambient indoor air at 0.6 %. This highlights the need for material optimization and shows that while ESA offers a promising pathway for CO<sub>2</sub> reduction, its practical application will depend on overcoming the technical hurdles (IEA, 2022; Voskian & Hatton, 2019).

#### **2.3.** Cost of capturing CO<sub>2</sub> from air

The economic feasibility of DAC technologies is a critical aspect of their potential deployment and scalability. Cost estimates for DAC vary widely based on technological maturity, energy sources and scale of development. Several studies and expert assessments offer a range of projected costs, highlighting the potential for cost reductions with technological advancements.

According to the "Direct air capture: a review" rapport published by SINTEF and Vista analyse (2022), DAC technology remains immature and costly with current expenses at the "Orca" plant estimated at 600 USD / tCO<sub>2</sub>, but there is an anticipated reduction in costs to 300 USD/ tCO<sub>2</sub> by 2025 and further to 100 USD / tCO<sub>2</sub> by 2050. It underscores the high variability in costs estimates, influenced by both capital and operational expenditures (CAPEX & OPEX), remaining uncertain due to limited deployment of facilities (Bisotti et al., 2023). The IEA provided levelized costs values (Table 1) along with noting specific cost ranges for both L-DAC (95-230 USD/tCO<sub>2</sub>) and S-DAC (100-600 USD/tCO<sub>2</sub>) (IEA, 2022).

Other studies provide a historical overview of the costs estimations before proposing estimates from subsequent analyses. Leading to 150-250 (CO<sub>2</sub> assuming use of hydroxides and solar energy for regeneration, with more optimistic scenarios at 53-127 /(CO<sub>2</sub> (Erans et al., 2022). This can only highlight the need for more research, development, and testing, to intime obtain precise techno-economic data, for this greenhouse gas mitigation pathway, leading to less atmospheric CO<sub>2</sub> and synthesized fuels.

# **3.** Overview of hydrogen production technologies

Hydrogen being a versatile energy carrier can be produced from various resources, both nonrenewable and renewable such as fossil fuels and water. Currently hydrocarbon reforming serves as the most developed and commonly used technology, fulfilling nearly the entire hydrogen demand. In fact, according to Nikkolaidis & Poulikkas (2017), hydrogen was produced 48% from natural gas, 30 % from heavy oils and 18% from coal (Nikolaidis & Poullikkas, 2017), which means that fossil fuels still dominate the world hydrogen supply as the production cost correlate strongly to fuel prices. Hydrocarbon reforming is defined as the process where hydrocarbon fuel is converged into hydrogen though different reforming techniques. These reforming processes needs other reactants in addition to hydrocarbons, reactants such as either steam, which gives the endothermic reaction known as steam reforming, or oxygen which gives the exothermic reaction known as partial oxidation (POX). When these two are combined with a net enthalpy change of 0, the third reforming process occurs, called autothermal reforming (ATR) (Megia et al., 2021; Nikolaidis & Poullikkas, 2017).

# 3.1. Steam methane reforming

Steam methane reforming (SMR) is the most widely used hydrocarbon reformation, mostly due to there being more extensive industrial experience, no oxygen requirement, and the highest  $H_2$  yield for  $H_2$  production (Holladay et al., 2009). The process is shown in Figure 3.



Figure 3: Flow diagram of the SMR process (Nikolaidis & Poullikkas, 2017)

SMR involves a chemical reaction where methane interacts with steam in the steam reformer, to produce carbon monoxide and hydrogen shown in Equation 4.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 (Equation 4)

Carbon monoxide is then converted to carbon dioxide and additional hydrogen through the water-gas shift (WGS) reaction, shown in Equation 5.

$$CO + H_2O \rightarrow CO_2 + H_2$$
 (Equation 5)

In order to raise efficiency, where CO reacts with water in the presence of a catalyst. The overall SMR reaction is shown in Equation 6 (Megia et al., 2021).

$$CH_4 + 2H_2 O \rightarrow CO_2 + 4H_2$$
 (Equation 6)

This reaction is endothermic meaning that a large amount of heat is needed, normally these reactions carry out at temperatures between 850 and 900°C. At these high temperatures there is a need for expensive construction materials for the reformer to withstand the heat and pressure, as well as a high-performance catalyst to maximize hydrogen production and minimize formation of unwanted byproducts. Most commonly used is a nickel-based catalyst, producing a hydrogen rich gas stream. The removal of  $CO_2$  and other impurities is done by pressure swing adsorption, this leaves an up to 99,99 % pure hydrogen stream behind with a recovery of 70-95% (Megia et al., 2021; Younas et al., 2022). The advantages of SMR will be its high efficiency, economic viability with the most developed technology and infrastructure and the scalability with SMR being suitable for various industrial applications. The biggest disadvantage is the significant amount of  $CO_2$  produced, unless combined with carbon capture and storage technologies. Other disadvantages is the reliance on natural gas, a fossil fuel

which would not be suitable long term and the high energy demand, increasing operational costs (Nikolaidis & Poullikkas, 2017).

# 3.2. Partial oxidation

Partial oxidation (POX) as a hydrogen production process, involves the controlled oxidation of hydrocarbons in the presence of a limited oxygen supply. This process can be used for converting a wide range of hydrocarbon feedstocks, from lighter gasses like methane (CH<sub>4</sub>), to heavier feedstocks such as oil residues and even coal, to hydrogen and CO<sub>2</sub>.

The POX process operates at varying temperatures depending on the process type. Catalytic processes, suitable for the lighter hydrocarbons, typically run around 950°C, while non-catalytic processes, accommodating heavier and more complex hydrocarbons including coal, operate at higher temperatures (1150-1315°C). This versatility in feedstock compatibility makes the POX process valuable for industries with access to diverse hydrocarbon streams. POX differ from SMR in the use of pure oxygen in the process, to avoid nitrogen dilution in produced syngas. This oxygen requirement adds a significant capital cost to the POX setup. The catalytic and non-catalytic reforming processes are shown in Equations 7 and 8, respectively, where hydrocarbons react with oxygen to produce carbon monoxide and hydrogen. Following this, the WGS reaction (shown in Equation 5) helps increase the hydrogen yield by converting CO and water steam into additional hydrogen and CO<sub>2</sub>.

$$C_n H_m + \frac{1}{2n} O_2 \to nCO + \left(\frac{1}{2m}\right) H_2 \qquad \text{(catalytic)} \qquad \text{(Equation 7)}$$

$$C_n H_m + nH_2 O \to nCO + \left(n + \frac{1}{2m}\right) H_2 \qquad \text{(non-catalytic)} \qquad \text{(Equation 8)}$$

Different values for n and m are applied based on specific feedstock, for instance feed coal would be n = 1 and m = 0 applied to Equation 8, while methane would be n = 1 and m = 4 applied to Equation 7. A typical flow diagram for H<sub>2</sub> production are shown in Figure 4 (Nikolaidis & Poullikkas, 2017).



Figure 4: Flow diagram of a partial oxidation (POX) (Nikolaidis & Poullikkas, 2017)

The main advantage of POX is how versatile it can be in feedstock selection, with it being effective for heavier and less reactive hydrocarbons. This along with there already being proven technology and existing infrastructure to support and there not being a need for external energy. Disadvantages however will be the lower hydrogen purity with the purity being less than both SMR and ATR and may potentially require further processing, also the pollution similarly to SMR with a CO<sub>2</sub> emission that requires treatment or CCS technologies, there could also be some challenges regarding the operational challenges with the handling and processing of the heavier feedstock or catalyst deactivation (Nikolaidis & Poullikkas, 2017).

#### **3.3.** Autothermal reforming

The autothermal reforming (ATR) method efficiently produces hydrogen by combining the heat generating POX reaction, with the hydrogen enhancing SMR reaction (for methane), thereby combining the principles in a single reactor. In ATR, steam and oxygen are injected into a reactor where they interact with (in this case) methane, causing the POX reaction and SMR reaction to occur simultaneously, shown in Equation 9 for CH<sub>4</sub>.

 $CH_4 + \frac{1}{2}H_2O + \frac{1}{4}O_2 \rightarrow CO + \frac{3}{2}H_2$  (ATR reaction for CH<sub>4</sub> feedstock) (Equation 9) Flow diagram for the methane ATR is shown in Figure 5. The thermal efficiency ranges from 60–75% for feedstock CH<sub>4</sub>, and maximum hydrogen yield is up to 2.8 moles of hydrogen per mole CH<sub>4</sub> (Holladay et al., 2009; Nikolaidis & Poullikkas, 2017).



#### Figure 5: Flow diagram of ATR utilizing methane as feedstock (Nikolaidis & Poullikkas, 2017)

Advantages of ATR would be the flexibility of feedstock processing capability and the energy efficiency with the process being self-sustainable in terms of heat. The disadvantages here would be like the other two the CO<sub>2</sub> emissions, with a potential need for CCS to lower the carbon footprint, also the technological complexity of having both a reforming and an oxidation process in one system could give more operational challenges as well as catalyst degradation (Nikolaidis & Poullikkas, 2017).

#### 3.4. Renewable hydrogen production

Although the main feedstock for hydrogen production is currently derived from hydrocarbons, the shift towards renewable resources is becoming increasingly imperative. Renewable hydrogen, especially green hydrogen, can reduce the energy related CO<sub>2</sub> emissions significantly, contributing to the climate change mitigation. Green hydrogen is produced through the electrolysis of water, a process that splits water into hydrogen and oxygen using electricity. When this electricity is sourced from renewable energy sources such as solar energy, wind energy and hydropower, the hydrogen created are exceptionally clean, almost with no associated CO<sub>2</sub> emissions. Water, one of the most abundant resources on Earth, serves as the primary raw material in this process, positioning electrolysis as a potentially limitless source of clean energy (Bartels et al., 2010; Megia et al., 2021).

#### 3.5. Electrolysis

Electrolysis is the non-spontaneous chemical process carried out in an electrolyzer, where high-quality hydrogen is produced by the electrochemical conversion of water (H<sub>2</sub>O) into

hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>). A typical electrolyzer consists of two electrodes, the anode (positive) and the cathode (negative), submerged in an electrolyte, serving as the medium that for this ion exchange, while preventing the mixing of H<sub>2</sub> and O<sub>2</sub>. The most developed and commonly used technologies for water electrolysis include alkaline water electrolysis (AWE), proton-exchange membrane (PEM) electrolysis and solid oxide water electrolysis (SOE) (Nikolaidis & Poullikkas, 2017; Younas et al., 2022).

#### 3.5.1. Alkaline water electrolysis

AWE is a well-established method for hydrogen production, characterized by the use of two non-noble metal-based electrodes, typically nickel, submerged in an aqueous alkaline electrolyte, such as potassium hydroxide (KOH), with concentrations ranging from 20-30%. A diaphragm, usually asbestos made, separates the electrodes. This diaphragm allows the passage of water molecules and hydroxide ions, while preventing the gasses produced from mixing, ensuring both safety and efficiency(Carmo et al., 2013).

At the cathode water is reduced (Equation 10), forming hydrogen gas and hydroxide ions, further the hydroxide ions generated, migrate to the anode (Equation 11), where they are oxidized to produce oxygen and water. Leading this setup to efficiently regenerate water, while releasing oxygen and additional electrodes into the system (Holladay et al., 2009).  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$  (Reduction reaction) (Equation 10)  $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$  (Oxidation reaction) (Equation 11)

Following production, hydrogen and oxygen are separated from the liquid in a gas-liquid separation unit external to the electrolyzer. AWE typically achieves efficiencies of 50-60 % based on the lower heating value (LHV) of hydrogen, with current densities ranging from 100 – 300 mA/cm<sup>2</sup> (Holladay et al., 2009). A key advantage of AWE is the systems capability of producing hydrogen at a purity of approximately 99 %, making it ideal for various applications. It is also a well-established technology, remaining cost – effective compared to other electrolysis methods, due to the utilization of less expensive electrodes. Challenges for AWE include alkali fog production, with the fog generation, necessitating removal through desorption techniques to maintain operational integrity. The pressure maintenance balance being crucial to maintain, to prevent explosions and ensure efficient operation, and the AWE system usually slow startup and loading response, making integration with the fluctuating nature of renewable energy sources challenging. These systems generally require a steady power input for optimal functionality (Chi & Yu, 2018). This electrical energy consumption has hindered AWE systems widespread adoption due its less cost competitiveness compared

to other large-scale  $H_2$  production technologies. According to Nikkolaidis & Poullikkas (2017), the solution of using RES such as hydro, wind and solar, if the input can be steady, could give commercial alkaline electrolyzers producing 380 000 kg  $H_2$  annually with energy consumption at 53.4 kWh/kg  $H_2$  (Nikolaidis & Poullikkas, 2017).

#### 3.5.2. Proton exchange membrane

PEM electrolyzers utilize a solid polymer electrolyte, which serves dual roles. It separates the electrodes and acts effectively as a gas separator. This innovative setup facilitates the direct and efficient conversion of water into  $H_2$  and  $O_2$  without the need for a separate gas separation unit. The electrodes in PEM systems are typically coated with noble metals, such as platinum or iridium oxide. These materials are chosen for their superior catalytic properties, facilitating rapid reactions essential for efficient electrolysis.

At the anode, water is oxidized to oxygen, protons, and electrons, releasing the  $O_2$  gas while protons and electrons move towards the cathode. At the cathode, the protons and electrons recombine to form  $H_2$ . The overall reaction is shown in Equation 12 (Holladay et al., 2009).

$$H_2 O \rightarrow H_2 + \frac{1}{2}O_2$$
 (Overall PEM reaction) (Equation 12)

PEM electrolyzers are known for their low ionic resistances, allowing for higher current densities than traditional alkaline electrolyzers, typically achieving current densities greater than 1600 mA/cm<sup>2</sup>.Maintaining efficiencies between 55–70% (Holladay et al., 2009). Advantages of PEM electrolyzers is that no byproducts are produced, reducing the environmental impact, the compact and modular design making PEM electrolyzers suitable for various scales of operation, and the fast dynamic response to changes in power supply making PEM ideal for integration with RES. Its biggest hinder for wider adoption lies in the high cost of the noble metal catalysts (Chi & Yu, 2018).

#### 3.5.3. Solid oxide electrolysis cells

SOEC utilizes a solid oxide or ceramic electrolyte, that conducts oxygen ions from the cathode to the anode. The solid electrolyte allows for higher temperature operation, typically between 700–900°C. This high temperature allows a higher thermodynamic efficiency compared to AWE and PEM, due to lower power requirements from use of both heat and electricity. At the cathode water vapor is reduced to hydrogen and oxide ions ( $O^{2-}$ ), where the H<sub>2</sub> is collected and oxide ions mitigate to the anode where the oxidation reaction, releases O<sub>2</sub> and electrons. (Lahrichi et al., 2024; Megia et al., 2021). SOEC operates similarly to the

AWE system but differ in the way that hydrogen is left in unreacted water vapor instead of liquid water and unlike AWE which relies on liquid electrolytes, the solid electrolyte used is non-corrosive and does not undergo any liquid or flow distribution problems, thereby eliminating concerns regarding corrosion and electrolyte evaporation. However, the high temperature operation gives high material degradation thereby requiring use of costly materials and presents challenges in terms of duration and the fact that the generated hydrogen-water vapor mixture requires additional processes to obtain high purity hydrogen. Thus, SOEC technology is currently still under development (Chi & Yu, 2018; Holladay et al., 2009; Lahrichi et al., 2024).

#### 3.6. Overall comparison

Hydrogen production is important for the development of sustainable fuels. SMR, POX, ATR, AWE, PEM and SOEC, offer different potentials, efficiencies, technical maturities, costs, and suitability for renewable fuel production. Table 2 summarizes these parameters obtained from a wide range of data from various sources (Chi & Yu, 2018; Holladay et al., 2009; IEA, 2019; Nikolaidis & Poullikkas, 2017; Younas et al., 2022).

<i>Table 2: Comparative</i>	summary of hydrog	en production te	echnologies. Ad	lopted from (Chi	& Yu, 2018;
Holladay et al.	, 2009; IEA, 2019;	Nikolaidis & Po	ullikkas, 2017;	Younas et al., 2	022).

Technology	Potential	Cost (\$/kg)	Efficiency	Technical Maturity	Suitability for Renewable Fuel Production
SMR	High for large- scale production	2.9 \$/kg (incl. CCS costs)	74-85%	Commercially mature	Requires CCS and significant infrastructure
РОХ	Effective for heavier hydrocarbons	Slightly higher than SMR	60–75%	Commercially mature	Effective with CCS integration
ATR	Reduces overall energy needs	Comparable to SMR	60–75%	Near-term technology	Needs CCS and has potential with renewable heat
AWE	High scalability	6–7 \$/kg	60%	Commercially mature	Optimal with stable renewable energy
PEM	Excellent for variable renewable energy	8–10 \$/kg	55-70%	Increasingly viable	Ideal for renewable applications
SOEC	High efficiency with heat integration	12–15 \$/kg	60-80%	Under development	Promising for large-scale applications

To summarize, the traditional methods SMR and POX are the most cost-effective and technically mature, with wide infrastructure in place, but require CCS to mitigate their environmental impact, making them less viable for the use in renewable fuel production. ATR shares similar characteristics but is not fully commercial mature but offers enhanced energy efficiency. The electrolysis methods, AWE, PEM and SOEC, offer significant advantages for renewable fuel production, all through being more expensive due to higher material costs and advanced technology. AWE is the most affordable and mature of the options, making it suitable for large-scale applications, but a steady power input is required. This gives that PME and SOEC are the most promising for large-scale applications that integrate renewable energy sources.

# 4. Fuel synthesis

With hydrogen from electrolysis showing potential as a potential energy carrier, and DAC technology representing a new approach to CO<sub>2</sub> capture and utilization, a closed loop system can be created. A system that utilizes the renewable energy sources such as solar and wind, to use for hydrogen production and DAC, further using the H<sub>2</sub> and CO<sub>2</sub> for fuel production, would create an emission neutral fuel, like methanol and to mention some more, methane and ethanol (IEA, 2019). These fuels will act both as an alternative for fossil fuel produced fuels and give opportunities across the energy storage and transportation sectors. Ammonia on the other hand is synthesized from renewable hydrogen integrated with atmospheric nitrogen. Ammonia and methanol were specifically chosen for this study, due to their potentials in Norway with the large Norwegian maritime transportation sector in need of decarbonization options. Additionally, can e-methanol easily be integrated into existing infrastructure, reducing need of extensive modifications, offering a sustainable alternative to fossil fuels, supporting Norway's goals of reducing emissions and enhancing energy security. Renewable ammonia also offers advantages in a Norwegian context, firstly that it can operate as a hydrogen carrier, facilitating the transportation and storage of hydrogen, one of the critical challenges of hydrogen utilization, and can also be utilized as a sustainable maritime fuel. The already existing infrastructure for ammonia production and distribution in Norway can be adapted to accommodate renewable ammonia, minimizing the need for new investments.

#### 4.1. Renewable methanol

Renewable methanol, also called e-methanol, is a sustainable alternative to conventional methanol, produced by integrating renewable hydrogen with CO<sub>2</sub>. There are several methods for synthesizing renewable methanol, including direct synthesis and two-step synthesis.

#### 4.1.1. Two-step methanol synthesis

The two-step synthesis process involves an initial conversion of  $CO_2$  to carbon monoxide (CO) via the reverse water-gas shift (RWGS) reaction shown in Equation (13), followed by the synthesis of methanol from the CO and additional hydrogen.

$$CO_2 + H_2 \rightarrow CO + H_2O$$
 ( $\Delta H = 41.2 \text{ kJ/mol}$ ) (Equation 13)

This endothermic reaction is favored at high temperatures, with optimal conversion occurring around 800°C, where about 60% of CO<sub>2</sub> is converted to CO. Catalysts such as ZnO/Al<sub>2</sub>O<sub>3</sub> are crucial for achieving selective and efficient conversion (Anicic et al., 2014). Following the RWGS, the gas mixture is cooled, and water is removed via a flash separator,

leaving a mixture of CO, CO<sub>2</sub> and H<sub>2</sub>. Before the second reactor, additional hydrogen is added to maintain the stochiometric ratio required for methanol synthesis. In the second reactor, methanol is synthesized using a highly selective CU/ZnO catalyst, and three reactions occur simultaneously in the second reactor, RWGS shown in Equation (13), methanol synthesis from H<sub>2</sub> and CO<sub>2</sub> shown in Equation (14) and synthesis of methanol from syngas, shown in Equation (15).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$
 ( $\Delta H = -49.2 \text{ kJ/mol}$ ) (Equation 14)  
 $CO + 2H_2 \rightleftharpoons CH_3OH$  ( $\Delta H = -90.4 \text{ kJ/mol}$ ) (Equation 15)

Post reaction, the mixture is further cooled to 30°C and phases are separated in another flash separator. Non-reactive components are recycled back to the second reactor or purged for combustion: The liquid phase containing methanol, water and dissolved gasses is distilled to separate methanol in multiple columns, utilizing energy from gas combustion to power the RWGS reactor (Anicic et al., 2014).

#### 4.1.2. Direct synthesis from H<sub>2</sub> and CO<sub>2</sub>

The direct synthesis of methanol involves the catalytic reaction of  $H_2$  and  $CO_2$  in a single step. This overall equation is shown in Equation 14 (Borisut & Nuchitprasittichai, 2019). In this exothermic reaction, a mixture of  $CO_2$  and  $H_2$  in a 1:3 ratio, is directly fed into the reactor, utilizing a Cu/ZnO catalyst at high pressures (50-100 bar) and operating under high temperatures (200- 300 °C), in optimized conditions to maximize yield and selectivity of methanol, while ensuring the stability of the catalyst. This direct conversion path, achieves a high selectivity and conversion rate for methanol, but also produces a significant amount of CO. This method is valued for its simplicity and potential lower energy requirements compared to the two-step process, through it requires precise control of reaction conditions to maximize yield and selectivity (Anicic et al., 2014).

#### 4.1.3. Cost competitiveness of renewable methanol

Renewable methanol production costs are currently significantly higher, than those of fossil fuel-based methanol production, which ranges from 100-250/t. However, with the lowest cost feedstocks and improvements in production processes, the cost of producing renewable methanol, from CO<sub>2</sub> and H<sub>2</sub> could approach the current cost and price of fossil fuel-derived methanol. For this cost to reach the lower level of conventional methanol, there needs improving of the competitiveness of e-methanol. The large-scale production of e-methanol depends on the availability of inexpensive green hydrogen and CO<sub>2</sub>, as well as the

capital cost of the plant. The main cost drivers are the renewable power needed to generate the required  $H_2$  and the utilization rates of the electrolyzers. This gives that currently e-methanol remains costly to produce, but the decreasing costs from renewable electricity from wind and solar energy, could indicate significant future cost reductions. This will mainly be the case when innovations in electrolyzers further aid reducing production costs (IRENA & METHANOL INSTITUTE, 2021).

Another way to make e-methanol more cost competitive, could be the utilization of CO<sub>2</sub> from another, cheaper source than DAC, although DAC shows the highest potential, its costs need to decrease substantially for wide implementation. Again, requiring extensive research and public attention towards developing these technologies, for the best possible e-methanol production cost. A solution proposed was the combining of production facilities, combining e-methanol with bi-methanol in a single facility. In this hybrid plant, the excess CO<sub>2</sub> generated from bio-methanol production, could be used in e-methanol production, optimizing source and reducing overall costs (IRENA & METHANOL INSTITUTE, 2021).

#### 4.1.4. Future markets for e-methanol

The future market for renewable methanol, will expand significantly in the future, with demand for methanol rising, and global efforts to mitigate climate change intensify, there will be a range of utilization areas for e-methanol. Including industrial applications, biodiesel production, energy storing and grid balancing, aviation and the integration to the maritime transport sector (IRENA & METHANOL INSTITUTE, 2021). Shipping companies are committing to the sustainable change, with companies such as shipping giant Maersk welcoming their second methanol enabled vessel to join their ocean fleet, highlighting that this is just the beginning, with goals set at making all their ships methane enabled (MAERSK, 2024).

## 4.2. Renewable ammonia

Ammonia, with its pivotal role in global agriculture, is important to integrate to the green energy landscape. Traditional ammonia production is highly energy intensive and reliant on fossil fuels, primarily natural gas and coal, through hydrogen feedstock use from SMR and POX. This section discusses the shift towards renewable ammonia production, utilizing green hydrogen derived from PEM or SOEC, and nitrogen separated from air, highlighting innovative production pathways and the potential applications of ammonia as a sustainable fuel. Renewable ammonia production from wind or solar energy, remains limited (0.02 Mt NH<sub>3</sub>/year) but is expected to grow. According to "Innovation Outlook: Renewable Ammonia" from IRENA & AEA(2022), renewable ammonia production is projected to reach 15 Mt by 2030, representing about 8 % of global production, indicating a strong industry shift towards sustainable production methods, further the report highlights the existence of around 80 Mt capacity for renewable ammonia production, and further suggest that for the 1.5 °C scenario, the production capacity will need to 566 Mt by 2050 (IRENA & AEA, 2022).

#### 4.2.1. Adapted Haber-Bosch process for renewable ammonia synthesis

The Haber-Bosch process, historically used for ammonia production, combines nitrogen (N<sub>2</sub>) and H<sub>2</sub> gasses in the presence of an iron-based catalyst under high temperature (450-500 °C) and pressure (200 bar), this chemical reaction is shown in Equation 17 (Giddey et al., 2017).

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
 ( $\Delta H = -46 \text{ kJ/mol}$ ) (Equation 17)

For the renewable adaption, the Haber-Bosch process undergoes significant adaptions to incorporate green hydrogen. The green hydrogen either comes from PEM electrolysis or SOEC, that offer high efficiency and dynamical operation from fluctuating renewable electricity. The nitrogen is separated from air using air separation unit (ASU), where air is processed using methods, pressure-swing adsorption (PSA) or cryogenic distillation, hereby leaving pure nitrogen. Further are N<sub>2</sub> and H<sub>2</sub> mixed in a stoichiometric ratio of 1:3. The mixed gasses then undergo compression to meet high Haber-Bosch pressure requirements, before synthesized (Giddey et al., 2017). Process is illustrated in Figure 6.



Figure 6: Ammonia synthesis from (a) different fossil feedstocks, and (b) renewable ammonia synthesis from water and air. Obtained from (Giddey et al., 2017).

#### 4.2.2. Costs competitiveness of renewable ammonia

The production cost of renewable ammonia and fossil-based ammonia has a high difference, all through advancements in technologies are expected to change this in coming decades. For renewable ammonia plants, the production cost currently ranges between \$720-\$1400/ton. However, these costs are projected to fall to a price range of \$310- \$610/ton by 2050. In comparison, the current production cost for natural gas or coal based (SMR, POX) range from \$110 to \$340/ton. Incorporating CCS to these would add an additional amount of \$100-\$150/ton, resulting in low emission fossil fuel based ammonia costs of \$210-\$490/ton (IRENA & AEA, 2022). The key factor influencing cost of renewable ammonia is the cost of renewable hydrogen production, which represents 90 % of the ammonia production cost, while the other processes (nitrogen separation, Haber-Borsch process) only contribute a minor fraction in comparison. Future cost reductions in renewable H<sub>2</sub> production will be achieved through decreases in renewable energy costs, reduced electrolyzer cost and improvements in efficiency (IRENA & AEA, 2022).

#### 4.2.3. Future markets for decarbonized ammonia

The future markets for decarbonized ammonia appear promising, particularly within sectors transitioning towards greener energy solutions. As IRENA & AEA (2022) suggests ammonia is increasingly considered a viable zero-carbon fuel option for the maritime sector due to its higher energy density compared to hydrogen and ease of storage and transport. This is underscored by planned deployments of ammonia-fueled ships and engines expected by 2025 (IRENA & AEA, 2022). Furthermore, the commercial developments are outlined by Øytese K. Å (2021) in the publication from "Energi og Klima", where they highlighted major companies desire to push this decarbonizing agenda. Yara a Norwegian fertilizer production company with their goal to produce green hydrogen and green ammonia, joined "The Castor Initiative" in 2021, an ambitious endeavor to develop an ammonia fueled tanker by 2025. Additionally did the Danish company Copenhagen Infrastructure Partners, together with shipping giant Maersk announce their plans for the establishment of Europe largest green ammonia plant, planning to build a 1 GW (Giga Watt) electrolysis facility, expected to reduce CO<sub>2</sub> emissions by approximately 1.5 Mt / year. Additionally shipping company DFDS (Det Forenede Dampskips-Selskap) promising to utilize this green ammonia from 2026 (Øystese K. Å, 2021). This signifies an accelerating industrial momentum towards ammonia-based

solutions. Even supported by policies aiming to foster zero-emission environments, like Norway's goal for emission free world heritage fjords by 2026, which will likely increase the demand for green ammonia and methanol (Øystese K. Å, 2021).

# 5. Conclusion and future works

This literature has comprehensively explored the integration of renewable energy sources, direct air capture (DAC) technologies and advanced renewable hydrogen production processes with synthesis of renewable methanol from H<sub>2</sub> and captured CO<sub>2</sub>, and synthesis of ammonia from H<sub>2</sub> utilization. The findings indicate that integrating renewable energy sources, particularly solar and wind energy, with DAC systems is technically feasible and has the potential to reduce the carbon intensity of fuel production processes. This feasibility will be continuously improving by the increasing availability and decreasing costs of these renewable energy sources.

The potential for PEM and SOEC electrolyzers to produce green hydrogen on a large scale is particularly promising. These electrolyzers offer high efficiency and dynamic operation making them well suited for integration with fluctuating electricity supply. The development of renewable hydrogen technologies is crucial for climate change mitigation, with hydrogen serving as an essential component for both direct utilizations, in the long term, when sufficient infrastructure is in place, and in the near term to produce synthesized fuels.

Regarding the fuel pathways examined, renewable methanol and ammonia stood out due to their potential to replace fossil fuels in critical sectors. Methanol synthesis using hydrogen produced via PEM electrolysis and captured CO<sub>2</sub> from DAC would be identified as the most viable pathway due to its lower technological barriers, existing market infrastructure and lower production costs. Especially for the Norwegian context, where e-methanol and ammonia both are relevant due to their compatibility with existing infrastructure, supporting decarbonization efforts in the maritime sector, which for Norway with long coastlines and broad maritime activities is very relevant.

Advancements in hydrogen production, especially the scalability and decreasing cost of electrolyzers will be essential to successfully employ these sustainable fuels. Research across all sectors of renewable synthesized fuel production will be needed for the cost competitiveness and feasibility of successfully integrating these renewable pathways to our current time.

Future works will be crucial in deciding the future of these endeavors, it is important to focus on researching on enhancing the efficiency of both hydrogen production and DAC technologies. The development of more efficient electrolyzers and improvement of DAC sorbets could be the research angle to this.

Additionally, the need to reduce the high costs associated with renewable energy production especially hydrogen and DAC, as well as focus on the optimization of the fluctuating renewable energy sources, with specific attention to the continuous development and improvements of energy storage systems, hopefully to someday solve this issue.

Finally encourage governments and policy makers to implement subsidies to support the renewable development and develop robust regulatory framework to promote the use of renewable fuels and facilitate DAC integration.

By addressing these areas, Norway can advance its goals for reducing GHG emissions, enhancing energy security and positioning itself as a leader in sustainable fuel production. The successful implementation of these technologies will contribute to global efforts to combat climate change and transition to a sustainable energy future.

Further work to this thesis would be, a techno-economic analysis, to access the economic viability of the whole pathway from electricity source to final fuel, simulation work, creating simulations models to predict the performance and costs of integrated renewable energy sources with DAC and fuel synthesis systems, and lastly conduct detailed lifecycle assessments to evaluate environmental impacts of proposed fuel production pathways, by analyzing the carbon footprint and resource use.

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