


Review

# Methane Removal from Air: Challenges and Opportunities

Jin Wang \*  and Qinghua Peter He

Department of Chemical Engineering, Auburn University, Auburn, AL 36849, USA; qhe@auburn.edu

\* Correspondence: wang@auburn.edu

**Abstract:** Driven by increasing greenhouse gas (GHG) concentrations in the atmosphere, extreme weather events have become more frequent and their impacts on human lives have become more severe. Therefore, the need for short-term GHG mitigations is urgent. Recently, methane has been recognized as an important mitigation target due to its high global warming potential (GWP). However, methane's low concentration in the atmosphere and stable molecular structure make its removal from the air highly challenging. This review first discusses the fundamental aspects of the challenges in atmospheric methane removal and then briefly reviews the existing research strategies following the mechanisms of natural methane sinks. Although still in its infancy, recent research on methane removal from the air holds great potential for slowing down global warming. At the same time, it is important to carefully examine the energy consumption of these methane removal strategies and whether they will be able to achieve net GHG reduction. In addition, due to the scale of methane removal from the air, any potential solution's environmental impacts must be carefully evaluated before it can be implemented in practice.

**Keywords:** global warming potential; intractable methane emissions; natural methane sink; photocatalytic reaction; methanotroph; mass transfer limitation

## 1. Introduction: The Necessity of Methane Removal from Air

As greenhouse gases (especially carbon dioxide or CO<sub>2</sub> and methane or CH<sub>4</sub>) in the atmosphere keep increasing, so does global temperature. In 2022, global CO<sub>2</sub> emissions from industrial processes and fuel combustion reached a new all-time high of 36.8 Gt (giga metric ton), and global CH<sub>4</sub> emissions from both natural processes and human activities were 589 Mt (million metric ton) [1]. At the same time, the average global temperature reached a new record high in July 2023. Associated with the increasing global temperature, extreme weather events such as heat waves, heavy precipitation, droughts, and tropical cyclones have become more frequent and their impacts on human lives have become more severe. Therefore, there is an urgent need to mitigate GHG emissions, especially for short-term mitigations.

In 2022, the global average atmospheric concentration was 417.06 ppm (part per million) for CO<sub>2</sub>, and 1911.8 ppb (part per billion) or ~1.91 ppm for CH<sub>4</sub> [2]. Although CH<sub>4</sub> in the atmosphere is far less abundant than CO<sub>2</sub>, its global warming potential (GWP) is significantly higher than CO<sub>2</sub>. In other words, CH<sub>4</sub> traps far more heat than CO<sub>2</sub>. The GWP of CO<sub>2</sub> is 1. The GWP of CH<sub>4</sub> is 84–87 on a 20-year scale and 27–36 on a 100-year time scale [1,3]. This is because CH<sub>4</sub> has a shorter lifetime than CO<sub>2</sub> in the atmosphere. CH<sub>4</sub> emitted today lasts about a decade in the atmosphere on average [3], while CO<sub>2</sub> would last much longer: in the range of 300–1000 years [4].

Due to the much higher concentration of CO<sub>2</sub> in the atmosphere, the major GHG reduction efforts have been almost entirely focused on CO<sub>2</sub>, especially in the industrial sectors. Only recently, the prominent and growing role of CH<sub>4</sub> emission in climate change has been recognized. In fact, studies have shown that methane contributes about 0.5 °C (or nearly half) of the observed 1.1 °C present-day warming above the pre-industrial



**Citation:** Wang, J.; He, Q.P. Methane Removal from Air: Challenges and Opportunities. *Methane* **2023**, *2*, 404–414. <https://doi.org/10.3390/methane2040027>

Academic Editor: Patrick Da Costa

Received: 12 September 2023

Revised: 19 October 2023

Accepted: 23 October 2023

Published: 1 November 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

temperature [5–7]. As a result, it is now broadly accepted that CH<sub>4</sub>, in addition to CO<sub>2</sub>, should be a critical focus for slowing global warming by 2050 [6–11].

Because of CH<sub>4</sub>'s high global warming potential and relatively short half-time in the atmosphere, CH<sub>4</sub> removal can contribute substantially to near-term climate mitigation [8,11–14]. Numerous studies have shown the outsized value of CH<sub>4</sub> mitigation in slowing down global warming over the next few decades [6,8,9,12,13]. Specifically, recent studies predict that a removal of 300 Mt of CH<sub>4</sub> (25.8 billion tons CO<sub>2</sub> equivalence on a 20-year scale) can slow global warming by 0.21–0.22 °C in 2050, a magnitude that can have a major positive impact on our climate future [8,11].

Among the 589 Mt of CH<sub>4</sub> released in 2022, 233 Mt was released by natural sources (around 40% of the total), while the rest (356 Mt) was from human activities (also known as, anthropogenic emissions, around 60% of the total). The primary anthropogenic sources are agriculture (142.3 Mt), the energy sector (133 Mt, including oil, natural gas, coal, and biofuels industries) and waste (70.8 Mt) [1]. Currently, a range of technological advancements have been attempted or proposed to reduce CH<sub>4</sub> emissions, especially for reducing emissions from “tractable” (easier to mitigate) anthropogenic sources such as energy and mining sectors [8,14,15]. However, CH<sub>4</sub> emissions from “intractable” (hard to mitigate) anthropogenic sources such as agriculture are much more difficult to deal with. Most agricultural CH<sub>4</sub> emissions are from scattered, non-point sources, such as rice paddy fields, cattle, sheep, and other ruminants, where complete emission reduction is not likely to be achieved. In addition, it has been shown that many CH<sub>4</sub> emission reduction approaches could result in increased nitrous oxide (N<sub>2</sub>O) emissions, which have a GWP of 273 on a 100-year time scale [3]. For example, a meta-analysis of 52 studies on rice farming practices for CH<sub>4</sub> reduction showed that with a 53% reduction in CH<sub>4</sub> emission, there was a 105% increase in N<sub>2</sub>O emission and 4% reduction in rice yield [15]. In addition to the “intractable” CH<sub>4</sub> emissions, global warming could significantly increase CH<sub>4</sub> emissions from permafrost systems and other sources. Therefore, it has been suggested that atmospheric CH<sub>4</sub> removal is necessary to offset continued CH<sub>4</sub> emission and limit global warming, especially for emissions from natural sources and “intractable” sources [16–18].

In this work, we first briefly discuss the fundamental challenges associated with CH<sub>4</sub> capture from air. Next, for methane removal, we provide an overview of the natural CH<sub>4</sub> sinks, followed by the state-of-the-art on the potential technologies for CH<sub>4</sub> removal. Finally, we discuss the key factors to consider for the future development of CH<sub>4</sub> removal technologies.

## 2. Challenges in Methane Removal from Air

Methane removal from air is highly challenging, mainly due to the following two reasons: the low concentration of methane in the atmosphere, and the highly stable molecular structure of methane. Below we discuss the implications of these factors on methane capture technologies.

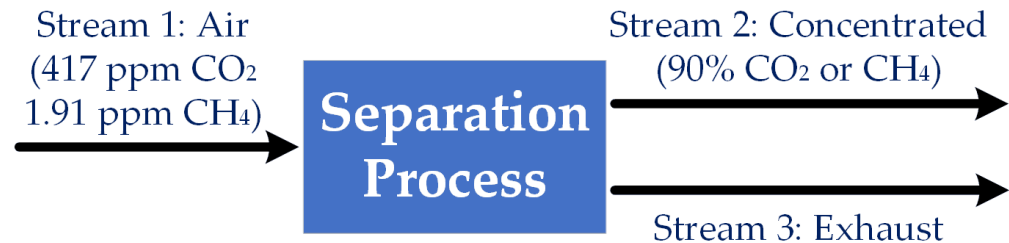
### 2.1. Minimum Thermodynamic Work for Separation

Compared to CO<sub>2</sub>, the relative scarcity of CH<sub>4</sub> in the atmosphere (1.91 ppm) leads to a higher minimum thermodynamic energy requirement to separate CH<sub>4</sub> from air. As illustrated in Figure 1, we consider a scenario similar to CO<sub>2</sub> capturing from air, i.e., isolating dilute CH<sub>4</sub> from the ambient air and separating it into a higher purity stream. The absolute minimum thermodynamic work of separation (MTWS) for the process depicted in Figure 1 can be calculated by assuming ideal gas mixing in a reversible, isothermal, and isobaric process [16]:

$$W_{min} = RT[(n_{2c} \ln y_{2c} + n_{2r} \ln y_{2r} + n_{3c} \ln y_{3c} + n_{3r} \ln y_{3r}) - (n_{1c} \ln y_{1c} + n_{1r} \ln y_{1r})] \quad (1)$$

where  $R$  and  $T$  are the ideal gas constant and temperature (K),  $n_{ij}$  is the molar flow rate of a specific component  $j$  in stream  $i$ , and  $y_{ij}$  is the mole fraction of component  $j$  in stream  $i$ .  $j$  can be  $c$  (the species to be separated, i.e., CO<sub>2</sub> or CH<sub>4</sub>) or  $r$  (the rest of the species in the

stream).  $i$  can be the inlet stream (1), the concentrated stream (2) or the exhaust stream (3). No real process could operate by only inputting the theoretical minimum work, but the minimum work provides a bottom line for comparing different scenarios.



**Figure 1.** Schematic of a generic air separation process for capturing CO<sub>2</sub> or CH<sub>4</sub>.

Equation (1) applies to both CO<sub>2</sub> and CH<sub>4</sub> capture from air. The current concentration of CO<sub>2</sub> in the atmosphere is 417.06 ppm, while that of CH<sub>4</sub> is 1.91 ppm. If we assume the concentrated stream contains 90% (i.e., 0.9 mole fraction) of the component to be captured (CO<sub>2</sub> or CH<sub>4</sub>) with 70% capture fraction (i.e.,  $n_2 y_{2c} = 0.7 n_1 y_{1c}$ , where  $n_2 = n_{2c} + n_{2r}$  and  $n_1 = n_{1c} + n_{1r}$ ) then the MTWS is 19.59 kJ/mol (or 445 J/g) for CO<sub>2</sub> and 32.93 kJ/mol (or 2053 J/g) for CH<sub>4</sub> at 298 K. Using the gas component's warming impact as the basis for comparison, we should normalize the MTWS for CH<sub>4</sub> to an equivalent amount of CO<sub>2</sub>. Using a GWP of 86 on a 20-year time scale for methane, its MTWS becomes 23.87 J/gCO<sub>2</sub>eq, which is only 5.4% of that for CO<sub>2</sub>. In other words, to achieve the same environmental impact of slowing down global warming, the MTWS required for CH<sub>4</sub> capture is only one-twentieths of that for CO<sub>2</sub> capture, which suggests that CH<sub>4</sub> capture is a favorable route over CO<sub>2</sub> capture in terms of MTWS. It is worth noting that if we consider CH<sub>4</sub> capture from locations with elevated CH<sub>4</sub> concentration, such as 500 ppm, the MTWS required further reduces to 19.13 kJ/mol CH<sub>4</sub>, or 13.87 J/gCO<sub>2</sub>eq.

### 2.2. The Scale of the Problem: Volume of Air to Be Processed

Due to the low methane concentration in the atmosphere, huge amounts of air must be processed in order to reduce methane's global warming impact. Using the average concentration of CH<sub>4</sub> in the atmosphere (1.91 ppm) and average temperature (17 °C), 1.55 bcm (billion cubic meter) of air must be processed in order to remove one tonne of methane, assuming a 50% removal rate. Whether it is feasible to process such vast amounts of air has raised concerns regarding the practicability of methane removal from air [18,19]. If removing methane from the air costs a significant amount of energy (which is usually associated with CO<sub>2</sub> emission) such that it cancels the global warming reduction obtained from methane removal, it would be better to pursue other routes instead of methane removal from the air.

To address this concern, it has been suggested that methane removal from the air should start with locations with elevated CH<sub>4</sub> concentration (e.g., 100 ppm or higher), such as landfills or manure lagoons. With higher atmospheric CH<sub>4</sub> concentration, both the minimum thermodynamic work required and the volume of air to be processed can be reduced significantly. For sites with 500 ppm CH<sub>4</sub> in the atmosphere, only 5.95 mcm (million cubic meter) of air must be processed to remove one tonne of CH<sub>4</sub>, an over 99.6% reduction compared to the case of 1.91 ppm. In the U.S. alone, there are many thousands of emission sites with 500 ppm or above methane concentrations [20]. For the methane emission sites, methane removal from the air can be justified as the elevated methane concentrations could enable cost and energy efficient reduction in global warming impact.

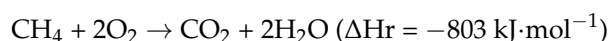
### 2.3. Methane Conversion vs. Capture

Because of the high GWP of methane, it is not necessary to capture CH<sub>4</sub> (i.e., separate and remove CH<sub>4</sub>) from the atmosphere to reduce its warming impact. Instead, CH<sub>4</sub> can be oxidized to CO<sub>2</sub> through catalytic oxidation or converted to CO<sub>2</sub> and biomass (a co-benefit)

through bacteria without separation. If we consider the complete oxidation of CH<sub>4</sub> to CO<sub>2</sub>, then the reduction of warming impact from CH<sub>4</sub> conversion would be 85/86 = 99% of that from CH<sub>4</sub> removal on a 20-year basis, and 33/34 = 97% on a 100-year basis (using 86 and 34 as CH<sub>4</sub> GWP on 20- and 100-year scales, respectively) [18]. Because of such a small difference in the reduction in warming impact between conversion and capture (separation and removal), as well as the simplicity of conversion compared to capture, most existing technologies are for CH<sub>4</sub> conversion instead of CH<sub>4</sub> capture.

#### 2.4. Consideration in Methane Oxidation

**Thermodynamic considerations:** In theory, CH<sub>4</sub> can be oxidized, without the need for capture, in a thermodynamically favorable reaction as shown below,



This exothermal reaction enables us to use natural gas for cooking and heating. However, the flammable range of methane in air is 5.3–14%. Therefore, it is impossible to flare methane even for the methane-rich sites (500–5000 ppm).

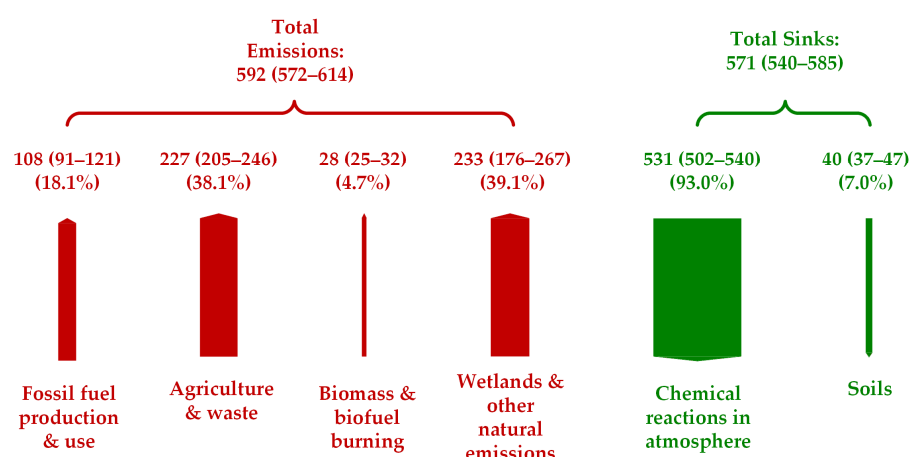
**Kinetic considerations:** Methane oxidation is very difficult to occur at typical atmospheric temperature and pressure conditions, despite its thermodynamic favorability. The symmetrical tetrahedral molecular structure of CH<sub>4</sub> is similar to that of diamond if one replaces the four “H” atoms with “C” atoms. This highly stable molecular structure results in a bond dissociation energy of 438.86 kJ/mol for CH<sub>4</sub> (g) → CH<sub>3</sub> (g) + H (g) [21]. Therefore, to make methane oxidation happen, highly effective catalysts are needed to significantly lower the activation energy barrier. In addition, the tetrahedral and non-polar methane molecular structure makes the binding of methane with the catalyst difficult, further complicating the conversion of methane from the air.

**Mass transfer considerations:** methane has a small solubility in water. Its Henry’s law constant for solubility is only 0.0014 mol/(kg·bar) at 25 °C, meaning that only 0.0014 mol (or 0.0225 g) of methane can be dissolved in 1 kg of water at a pressure of 1 bar or approximately 1 atm [22]. The solubility is not much higher in traditional organic solvents either (with a Henry’s law constant of 0.0391 mol/(kg·bar) in n-hexane, 0.0262 in acetone and 0.0226 in ethanol) [23]. These small solubilities make the traditional enrichment approaches infeasible due to the huge number of cycles required to achieve a concentrated methane stream. In addition, if methane oxidation happens in the liquid phase instead of the gas phase, such as in the case of biological methane conversion, then the small solubility will pose significant challenges in mass transfer, i.e., methane conversion from air would be mass transfer-limited, instead of kinetic-limited.

### 3. State-of-the-Art for Methane Removal from the Air

Figure 2 depicts the global methane budget for 2017, which has an estimated total methane emission of 592 Mt and a total methane sink of 571 Mt. Among all methane emissions, about 40% are from natural sources (wetlands, ocean, inland water, etc.), while 60% are from anthropogenic sources (agriculture, waste, fossil fuels, etc.). A world map showing different categories of methane emissions across different continents and countries can be found in [24]. Because the natural methane sinks cannot match the increasing emissions caused by human activities, the atmospheric methane concentration kept increasing from the pre-industrial level (~750 ppb) to about 1912 ppb in 2023, a two-and-a-half-fold increase. Another concerning observation is that the atmospheric concentration of hydroxyl radicals (OH, contributing to CH<sub>4</sub> destruction) has been stagnant or decreasing since 2007, which can help explain the increase in atmospheric methane since 2007 [24].

In this section, we first discuss the mechanisms of natural methane sinks, then a list of emerging technologies on methane removal from air, which in general aims to enhance the natural sinks.



**Figure 2.** 2017 Global Methane Budget in Mt (Adapted from [25]).

### 3.1. Natural Methane Sinks

As shown in Figure 2, natural methane sinks consist of chemical reactions in the atmosphere and biological conversions in soil and water [24]. Among atmospheric reactions, tropospheric hydroxyl radical [OH] contributes the most to natural methane removal (Reaction 1 below), accounting for almost 90% of annual total methane removal; tropospheric photolytic chlorine atom [Cl] contributes much less to methane removal, accounting for about 2.5% of annual total removal (Reaction 2) [24].  $\text{CH}_3\text{O}_2$  in the atmosphere is further converted to  $\text{O}_3$  and  $\text{CO}_2$  through a sequence of photochemical reactions [26]. Together, these atmospheric chemical reactions removed 531 Mt of methane (93% of the total 571 Mt removed methane) in 2017, as shown in Figure 2.



On the other hand, bacteria (both aerobic methanotroph and anaerobic archaea) in the soil and water provide the second-largest natural sink for atmospheric methane. In 2017, these biological sinks removed 40 Mt of methane (7% of 571 Mt total methane sink as shown in Figure 2) [25]. In total, both the atmosphere reactions and biological assimilations removed 571 Mt of methane in 2017. However, the total methane emission in 2017 was estimated to be 592 Mt, which resulted in a net increase in 21 Mt methane in the atmosphere in 2017 [25].

### 3.2. Potential Technological Methane Sinks

Technologies for methane removal from the air have been explored only recently, and no scalable technology exists today [18,27]. Methane removal from the air is inherently challenging because of its low concentration and stable tetrahedral structure. Below we discuss current research on methane removal technologies, which generally aim to enhance different natural methane removal pathways. Table 1 summarizes these different technologies.

**Table 1.** Representative technologies for  $\text{CH}_4$  capture from air.

Technology Pathway	Sub-Pathway	Approach	Reaction Locus	Gas Flow	Sample Reference
Chemical conversion	Photocatalytic oxidation	TiO <sub>2</sub> or Ag-ZnO	Gas–solid interface	Active or passive	[28–30]
	Photochemical oxidation	Iron-salt aerosols	Gas	Passive	[31,32]
	Adsorption–oxidation	Zeolites or Porous Polymer Network	Gas–solid interface	Active or passive	[10,33,34]

Table 1. Cont.

Technology Pathway	Sub-Pathway	Approach	Reaction Locus	Gas Flow	Sample Reference
Biological conversion		Biofilter	Within cell	Active or passive	[35,36]
		Soil amendments	Within cell	Passive	[37,38]

**Photocatalytic oxidation:** As discussed in Section 2.4, because CH<sub>4</sub> is so stable, its direct oxidation needs to overcome a very high activation energy, which is conventionally achieved through energy-intensive reaction conditions (e.g., high temperature and pressure), strong oxidants and/or effective catalysts. Photocatalysis, an alternative to traditional thermocatalysis, is a promising technology that has the potential to significantly reduce the thermodynamic barrier and reduce energy requirements (e.g., by operating under ambient conditions). In the stratosphere, photocatalytic reactions can remove 12–37 Mt methane per year [24]. The ultraviolet light reacts with oxygen molecules to form atomic oxygen, which can oxidize methane to CO<sub>2</sub> through a series of reactions. Photocatalysis also generates charge carriers that pre-activate CH<sub>4</sub> and substantially reduce the activation energy, allowing for uphill (i.e., thermodynamically unfavorable) reactions to proceed under ambient conditions, which cannot be achieved through conventional thermocatalysis. Researchers have examined how to speed up these photocatalytic reactions using zinc oxide (ZnO) or titanium oxide (TiO<sub>2</sub>). Both ZnO doped with Ag [28,29] and TiO<sub>2</sub> [30] have shown promising results on methane removal. Li et al. [39] provide a comprehensive review of the field. In particular, various products can be photocatalytically synthesized from CH<sub>4</sub>, including methanol, formaldehyde, ethanol, ethane, ethylene, acetone, benzene, etc. Li et al. also reviewed over 20 representative methane-converting photocatalysts, including their basic mechanisms, experimental conditions, main products, product rate, and product selectivity. It is worth noting that all technologies reviewed by Li et al. use CH<sub>4</sub> as the building block (to replace crude oil) for synthesizing various chemicals, thus focusing on high-CH<sub>4</sub>-concentration point sources such as shale gas. As a result, the extremely low concentration of CH<sub>4</sub> in the atmosphere may render these technologies (significantly) less effective or completely ineffective. Nevertheless, some of the photocatalytic technologies were suggested for atmospheric CH<sub>4</sub> destruction or removal. For example, it was suggested that if a thin layer of TiO<sub>2</sub> is painted on all the rooftops across the world, it could remove roughly 10 Mt of methane annually [18]. However, how this can be achieved on a scale has not been widely debated. In addition, its potential negative side effects and environmental impacts have not been studied. In summary, despite being highly promising, the photocatalytic oxidation approaches for atmospheric CH<sub>4</sub> removal are still in their infancy, and research has mainly focused on understanding the reaction mechanism [10,28,30,33,34]. To advance research in this technology, researchers who have been focusing on high-concentration CH<sub>4</sub> at point sources need to shift their focus to low-concentration atmospheric CH<sub>4</sub>, e.g., by changing experimental conditions in their laboratory research.

**Photochemical oxidation via Iron-salt aerosol:** In this route, the focus is to enhance the availability of reactive chlorine species in the troposphere. Specifically, iron-salt aerosols have been shown to enhance Cl generation and increase Cl sink by four to six folds [16]. However, the available results are generated in smog chambers and have not yet been empirically validated or tested in situ [30,39]. In addition, the safety of this approach has yet to be established. The potential environmental impact of iron-salt aerosols on air quality and ocean-activity must be carefully evaluated before any action can be taken [23].

**Adsorption–oxidation with zeolites:** Zeolites have been used for adsorption of N<sub>2</sub> (as in oxygen concentrator) and CO<sub>2</sub> from air (with aluminosilicate zeolites). It has been suggested that zeolite-based extraction of CH<sub>4</sub> is also feasible [16]. In fact, 87,000 zeolite structures have been screened for methane adsorption [34]. In addition, Cu, Fe, or other metal ions can be embedded in the zeolite to oxidize the sorbed methane to methanol or CO<sub>2</sub>. For example, Fe zeolites have been shown to oxidize methane at room temperature

to produce methanol [40], although the experiment was carried out with 10% CH<sub>4</sub> in He gas. In other words, the in situ performance of the adsorption–oxidation approach with air that contains very low concentrations of CH<sub>4</sub> and many impurities, such as NH<sub>3</sub>, has yet to be established.

**Biological assimilation:** In the natural biological methane sinks, CH<sub>4</sub> oxidation is catalyzed by highly selective and highly efficient enzymes at ambient temperature and pressure (methane monooxygenase for aerobic methanotrophs and methyl coenzyme M reductase for anaerobic archaea) without releasing toxic byproducts [41]. Another advantage of the biological CH<sub>4</sub> capture is that only about 50% (molar) of CH<sub>4</sub> is converted to CO<sub>2</sub>, while the other half is assimilated to produce microbial biomass (a co-benefit), which reduces the amount of CO<sub>2</sub> released back into the atmosphere. Biological methane conversion has a much longer history of study, although they were mostly studied as CH<sub>4</sub> mitigation from point sources (with >5% of CH<sub>4</sub>) rather than CH<sub>4</sub> removal from air [35,38]. For example, methane biofilter is a reliable and cost-effective technology for CH<sub>4</sub> removal from point emission sources [42–48]. Bio-covers are well-established methods to mitigate landfill CH<sub>4</sub> emissions [49]. With the highly effective biocatalyst (particulate methane monooxygenase) for methane oxidation, the key challenge to the biological route is substrate limitation caused by low concentrations of methane in the atmosphere and the small solubility of methane in the aqueous solution. Another serious concern is the production of more potent GHGs, such as N<sub>2</sub>O, associated with some biological methane mitigation approaches, which could completely wipe out the benefits of methane removal [10].

#### 4. Discussion

As summarized in Table 1, all the chemical routes of methane conversion either have reactions happening in the gas phase or on the gas–solid surface. The rate-limiting step of these approaches is usually in reaction kinetics, either caused by the high activation energy barrier or the difficulty in binding methane to the active catalyst sites. The ideal catalysts for these routes should be able to selectively bind methane at very low concentrations and in the presence of other impurities, as well as significantly lowering the activation energy barrier to break the C–H bonds in methane. Recent advancement in novel material design and discovery holds the potential to significantly improve the reaction rate and selectivity, therefore making catalytic methane removal from the air a feasible solution [50].

On the other hand, for the biological routes, nature has developed highly efficient and highly selective biocatalysts through evolution. The limiting step of the biological route is substrate availability caused by mass transfer limitation. Because of the low concentrations of methane in the atmosphere and its very small solubility in aqueous solution, biological methane conversion is limited by low concentrations of biocatalysts—the production of biocatalyst is limited by methanotrophs growth, which is limited by substrate supply due to mass transfer resistance. To overcome these limitations, high binding affinity with methane is needed to support methanotroph growth at very low methane concentrations, and novel bioreactor designs are needed to reduce mass transfer resistance and enhance substrate supply. For the high-affinity biocatalysts, He et al. [20] recently provided highly promising results on the identification of methanotroph that can grow at 500 ppm of CH<sub>4</sub> and directions for future biological methane removal solutions. For the bioreactor design, biofilm-based cultivation has emerged as a highly promising solution to enhance the mass transfer of gas substrate to microbes [50–55].

For both the chemical reaction routes and the biological conversion routes, a large volume of the air must be processed in order to remove methane from the atmosphere, even for sites with elevated methane concentrations (>500 ppm). The capital cost and energy requirement of processing this large volume of air must be considered for atmosphere methane removal technologies to be practical. It has been suggested that using electrical fans to drive air through removing device may not be feasible [18,19]. However, passive systems that use natural winds or solar updraft towers (SUT) could provide feasible solutions [56,57], especially for the sites with elevated methane concentrations [58,59].

Another important consideration is the potential unintended negative side-effects of these cutting-edge technologies. Many researchers have focused solely on the positive aspects of the technology under study in order to promote the technology, and have often neglected or did not pay adequate attention to its potential negative impacts, especially the ones on the environment and ecosystems. Other important considerations include scalability, technical support and maintenance, user training and adoption, long-term viability and commitment, regulatory compliance, public acceptance, disaster resilience, etc. Some of these considerations can be quite different for developed and developing countries. These holistic studies should consider the entire life cycle of the technology, similar to the life cycle assessment (LCA) of CO<sub>2</sub> removal technologies [60].

## 5. Conclusions

In the wake of the rising frequency of extreme weather events due to climate change, the importance and urgency of methane mitigation have recently been recognized. Given methane's high global warming potential, it has been suggested that both emission mitigation and methane removal from the air are necessary to slow down global warming over the next few decades. In particular, methane capture from the air appears to be the most promising route to mitigate the "intractable" methane emissions. Compared to methane mitigation technologies that address emissions with moderate to high methane concentrations (above 5% volumetric fraction), technologies for atmospheric methane removal have been explored only recently.

Following the mechanisms of natural methane sinks, potential methane removal technologies can be divided into two broad groups: chemical oxidation and biological assimilation, with each route holding great potential to help limit global warming. The chemical oxidation route is based on the fact that methane has a significantly higher global warming potential than carbon dioxide. Because of that, methane can be oxidized to carbon dioxide, instead of being captured from the air, to reduce its global warming impact. In fact, the existing methane removal approaches are all based on methane oxidation, instead of methane capture. Although exothermic methane oxidation is thermodynamically favorable, the challenges associated with reaction kinetics (due to methane's stable molecular structure) and mass transfer (due to the very low concentration in the air) are difficult to address. In addition, chemical oxidation of atmospheric methane must process a large volume of air due to the low concentration of methane in the atmosphere. In comparison, biological methane assimilation has the advantage of low energy consumption due to its occurrence at ambient temperature and pressure. In addition, biological methane assimilation can produce microbial biomass as a co-benefit, which also reduces the amount of carbon dioxide released back into the atmosphere. However, the biological route has its own challenges, such as productivity or throughput limited by the low concentrations of methane in the atmosphere and the small solubility of methane in aqueous solutions. For both chemical and biological routes, besides technological and economic factors, environmental factors must also be considered when evaluating different technologies. Therefore, holistic approaches, such as LCA, are recommended to assess their pros and cons comprehensively. In particular, an important baseline is that the energy consumption (usually associated with GHG emission) required for methane removal cannot exceed its impact on global warming reduction. Despite these challenges, recent advances in material design and synthetic biology suggest that the prospects of atmospheric methane removal are promising, especially for sites with elevated methane concentrations in the air.



**Author Contributions:** Conceptualization, J.W. and Q.P.H.; writing—original draft preparation, J.W.; writing—review and editing, Q.P.H. and J.W.; funding acquisition, J.W. and Q.P.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Genomic Science Program under Award Number DE-SC0019181, U.S. Department of Agriculture, National Institute of Food and Agriculture under Award Number 2023-67021-39643, National Science Foundation under Award Number NSF-CBET-2331602, and Alabama Department of Economic and Community Affairs under Award Number ADECA-1ARDEF22 03.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** No new data were created or analyzed in this study. Data sharing is not applicable to this article.

**Acknowledgments:** The authors would like to thank Mary Lidstrom (University of Washington) for her insights and helpful discussions on biological methane removal from the air.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the conceptualization and writing of the manuscript; or in the decision to publish the work.

## References

1. IEA Global Methane Tracker. 2023. Available online: <https://www.iea.org/reports/global-methane-tracker-2023> (accessed on 29 August 2023).
2. Theo Stein Greenhouse Gases Continued to Increase Rapidly in 2022. Available online: <https://www.noaa.gov/news-release/greenhouse-gases-continued-to-increase-rapidly-in-2022> (accessed on 29 August 2023).
3. EPA Understanding Global Warming Potentials. Available online: <https://www.epa.gov/ghgemissions/understanding-global-warming-potentials> (accessed on 29 August 2023).
4. Buis, A. The Atmosphere: Getting a Handle on Carbon Dioxide. Available online: <https://climate.nasa.gov/news/2915/the-atmosphere-getting-a-handle-on-carbon-dioxide/> (accessed on 29 August 2023).
5. Masson-Delmotte, V.; Zhai, P.; Pirani, A.; Connors, S.L.; Péan, C.; Berger, S.; Caud, N.; Chen, Y.; Goldfarb, L.; Gomis, M.I. Climate Change 2021: The Physical Science Basis. *Contrib. Work. Group I Sixth Assess. Rep. Intergov. Panel Clim. Chang.* **2021**, *2*. Available online: [https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC\\_AR6\\_WGI\\_FrontMatter.pdf](https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC_AR6_WGI_FrontMatter.pdf) (accessed on 11 September 2023).
6. Harmsen, M.; van Vuuren, D.P.; Bodirsky, B.L.; Chateau, J.; Durand-Lasserve, O.; Drouet, L.; Fricko, O.; Fujimori, S.; Gernaat, D.E.H.J.; Hanaoka, T. The Role of Methane in Future Climate Strategies: Mitigation Potentials and Climate Impacts. *Clim. Chang.* **2020**, *163*, 1409–1425. [\[CrossRef\]](#)
7. Ocko, I.B.; Naik, V.; Paynter, D. Rapid and Reliable Assessment of Methane Impacts on Climate. *Atmos. Chem. Phys.* **2018**, *18*, 15555–15568. [\[CrossRef\]](#)
8. Ocko, I.B.; Sun, T.; Shindell, D.; Oppenheimer, M.; Hristov, A.N.; Pacala, S.W.; Mauzerall, D.L.; Xu, Y.; Hamburg, S.P. Acting Rapidly to Deploy Readily Available Methane Mitigation Measures by Sector Can Immediately Slow Global Warming. *Environ. Res. Lett.* **2021**, *16*, 054042. [\[CrossRef\]](#)
9. Collins, W.J.; Webber, C.P.; Cox, P.M.; Huntingford, C.; Lowe, J.; Sitch, S.; Chadburn, S.E.; Comyn-Platt, E.; Harper, A.B.; Hayman, G. Increased Importance of Methane Reduction for a 1.5 Degree Target. *Environ. Res. Lett.* **2018**, *13*, 054003. [\[CrossRef\]](#)
10. Jackson, R.B.; Solomon, E.I.; Canadell, J.G.; Cargnello, M.; Field, C.B. Methane Removal and Atmospheric Restoration. *Nat. Sustain.* **2019**, *2*, 436–438. [\[CrossRef\]](#)
11. Abernethy, S.; O'Connor, F.M.; Jones, C.D.; Jackson, R.B. Methane Removal and the Proportional Reductions in Surface Temperature and Ozone. *Philos. Trans. R. Soc. A* **2021**, *379*, 20210104. [\[CrossRef\]](#)
12. Alvarez, R.A.; Pacala, S.W.; Winebrake, J.J.; Chameides, W.L.; Hamburg, S.P. Greater Focus Needed on Methane Leakage from Natural Gas Infrastructure. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 6435–6440. [\[CrossRef\]](#)
13. Rogelj, J.; Meinshausen, M.; Schaeffer, M.; Knutti, R.; Riahi, K. Impact of Short-Lived Non-CO<sub>2</sub> Mitigation on Carbon Budgets for Stabilizing Global Warming. *Environ. Res. Lett.* **2015**, *10*, 075001. [\[CrossRef\]](#)
14. Nisbet, E.G.; Fisher, R.E.; Lowry, D.; France, J.L.; Allen, G.; Bakkaloglu, S.; Broderick, T.J.; Cain, M.; Coleman, M.; Fernandez, J. Methane Mitigation: Methods to Reduce Emissions, on the Path to the Paris Agreement. *Rev. Geophys.* **2020**, *58*, e2019RG000675. [\[CrossRef\]](#)
15. Malozyomov, B.V.; Golik, V.I.; Brigida, V.; Kukartsev, V.V.; Tynchenko, Y.A.; Boyko, A.A.; Tynchenko, S.V. Substantiation of Drilling Parameters for Undermined Drainage Boreholes for Increasing Methane Production from Unconventional Coal-Gas Collectors. *Energies* **2023**, *16*, 4276. [\[CrossRef\]](#)

16. Jackson, R.B.; Abernethy, S.; Canadell, J.G.; Cargnello, M.; Davis, S.J.; Féron, S.; Fuss, S.; Heyer, A.J.; Hong, C.; Jones, C.D. Atmospheric Methane Removal: A Research Agenda. *Philos. Trans. R. Soc. A* **2021**, *379*, 20200454. [CrossRef]
17. Warszawski, L.; Krieglner, E.; Lenton, T.M.; Gaffney, O.; Jacob, D.; Klingenberg, D.; Koide, R.; Costa, M.M.; Messner, D.; Nakicenovic, N. All Options, Not Silver Bullets, Needed to Limit Global Warming to 1.5 °C: A Scenario Appraisal. *Environ. Res. Lett.* **2021**, *16*, 064037. [CrossRef]
18. Nisbet-Jones, P.B.R.; Fernandez, J.M.; Fisher, R.E.; France, J.L.; Lowry, D.; Waltham, D.A.; Woolley Maisch, C.A.; Nisbet, E.G. Is the Destruction or Removal of Atmospheric Methane a Worthwhile Option? *Philos. Trans. R. Soc. A* **2022**, *380*, 20210108. [CrossRef] [PubMed]
19. Lackner, K.S. Practical Constraints on Atmospheric Methane Removal. *Nat. Sustain.* **2020**, *3*, 357. [CrossRef]
20. He, L.; Groom, J.D.; Wilson, E.H.; Fernandez, J.; Konopka, M.C.; Beck, D.A.C.; Lidstrom, M.E. A Methanotrophic Bacterium to Enable Methane Removal for Climate Mitigation. *Proc. Natl. Acad. Sci. USA* **2023**, *120*, e2310046120. [CrossRef]
21. Lü, R.; Lin, J. A Interpretation of Stepwise Bond Dissociation Energies of CH<sub>4</sub>. *Comput. Theor. Chem.* **2014**, *1037*, 10–13. [CrossRef]
22. NIST NIST Chemistry WebBook, SRD 69. Available online: <https://webbook.nist.gov/cgi/cbook.cgi?ID=74-82-8> (accessed on 6 September 2023).
23. Lannung, A.; Gjaldbaek, J.C. The Solubility of Methane in Hydrocarbons, Alcohols, Water and Other Solvents. *Acta Chem. Scand.* **1960**, *14*, 1124–1128. [CrossRef]
24. Saunio, M.; Stavert, A.R.; Poulter, B.; Bousquet, P.; Canadell, J.G.; Jackson, R.B.; Raymond, P.A.; Dlugokencky, E.J.; Houweling, S.; Patra, P.K. The Global Methane Budget 2000–2017. *Earth Syst. Sci. Data* **2020**, *12*, 1561–1623. [CrossRef]
25. Jackson, R.B.; Saunio, M.; Bousquet, P.; Canadell, J.G.; Poulter, B.; Stavert, A.R.; Bergamaschi, P.; Niwa, Y.; Segers, A.; Tsuruta, A. Increasing Anthropogenic Methane Emissions Arise Equally from Agricultural and Fossil Fuel Sources. *Environ. Res. Lett.* **2020**, *15*, 071002. [CrossRef]
26. Li, Q.; Meidan, D.; Hess, P.; Añel, J.A.; Cuevas, C.A.; Doney, S.; Fernandez, R.P.; van Herpen, M.; Höglund-Isaksson, L.; Johnson, M.S.; et al. Global Environmental Implications of Atmospheric Methane Removal through Chlorine-Mediated Chemistry-Climate Interactions. *Nat. Commun.* **2023**, *14*, 4045. [CrossRef] [PubMed]
27. Ming, T.; Li, W.; Yuan, Q.; Davies, P.; De Richter, R.; Peng, C.; Deng, Q.; Yuan, Y.; Caillol, S.; Zhou, N. Perspectives on Removal of Atmospheric Methane. *Adv. Appl. Energy* **2022**, *5*, 100085. [CrossRef]
28. Chen, X.; Li, Y.; Pan, X.; Cortie, D.; Huang, X.; Yi, Z. Photocatalytic Oxidation of Methane over Silver Decorated Zinc Oxide Nanocatalysts. *Nat. Commun.* **2016**, *7*, 12273. [CrossRef]
29. Zhu, S.; Li, X.; Pan, Z.; Jiao, X.; Zheng, K.; Li, L.; Shao, W.; Zu, X.; Hu, J.; Zhu, J. Efficient Photooxidation of Methane to Liquid Oxygenates over ZnO Nanosheets at Atmospheric Pressure and near Room Temperature. *Nano Lett.* **2021**, *21*, 4122–4128. [CrossRef] [PubMed]
30. Thampi, K.R.; Kiwi, J.; Grätzel, M. Room Temperature Photo-Activation of Methane on TiO<sub>2</sub> Supported Molybdena. *Catal. Lett.* **1988**, *1*, 109–116. [CrossRef]
31. Ming, T.; de Richter, R.; Oeste, F.D.; Tulip, R.; Caillol, S. A Nature-Based Negative Emissions Technology Able to Remove Atmospheric Methane and Other Greenhouse Gases. *Atmos. Pollut. Res.* **2021**, *12*, 101035. [CrossRef]
32. Oeste, F.D.; de Richter, R.; Ming, T.; Caillol, S. Climate Engineering by Mimicking Natural Dust Climate Control: The Iron Salt Aerosol Method. *Earth Syst. Dyn.* **2017**, *8*, 1–54. [CrossRef]
33. Bracco, S.; Piga, D.; Bassanetti, I.; Perego, J.; Comotti, A.; Sozzani, P. Porous 3D Polymers for High Pressure Methane Storage and Carbon Dioxide Capture. *J. Mater. Chem. A Mater.* **2017**, *5*, 10328–10337. [CrossRef]
34. Kim, J.; Maiti, A.; Lin, L.-C.; Stolaroff, J.K.; Smit, B.; Aines, R.D. New Materials for Methane Capture from Dilute and Medium-Concentration Sources. *Nat. Commun.* **2013**, *4*, 1694. [CrossRef]
35. Smith, P.; Goulding, K.W.; Smith, K.A.; Powlson, D.S.; Smith, J.U.; Falloon, P.; Coleman, K. Enhancing the Carbon Sink in European Agricultural Soils: Including Trace Gas Fluxes in Estimates of Carbon Mitigation Potential. *Nutr. Cycl. Agroecosyst* **2001**, *60*, 237–252. [CrossRef]
36. Price, S.J.; Sherlock, R.R.; Kelliher, F.M.; McSeveny, T.M.; Tate, K.R.; Condon, L.M. Pristine New Zealand Forest Soil Is a Strong Methane Sink. *Glob. Chang. Biol.* **2004**, *10*, 16–26. [CrossRef]
37. Cáceres, M.; Dorado, A.D.; Gentina, J.C.; Aroca, G. Oxidation of Methane in Biotrickling Filters Inoculated with Methanotrophic Bacteria. *Environ. Sci. Pollut. Res.* **2017**, *24*, 25702–25712. [CrossRef]
38. La, H.; Hettiaratchi, J.P.A.; Achari, G.; Dunfield, P.F. Biofiltration of Methane. *Bioresour. Technol.* **2018**, *268*, 759–772. [CrossRef]
39. Li, X.; Wang, C.; Tang, J. Methane Transformation by Photocatalysis. *Nat. Rev. Mater.* **2022**, *7*, 617–632. [CrossRef]
40. Snyder, B.E.R.; Vanelderden, P.; Bols, M.L.; Hallaert, S.D.; Böttger, L.H.; Ungur, L.; Pierloot, K.; Schoonheydt, R.A.; Sels, B.F.; Solomon, E.I. The Active Site of Low-Temperature Methane Hydroxylation in Iron-Containing Zeolites. *Nature* **2016**, *536*, 317–321. [CrossRef] [PubMed]
41. Lawton, T.J.; Rosenzweig, A.C. Methane-Oxidizing Enzymes: An Upstream Problem in Biological Gas-to-Liquids Conversion. *J. Am. Chem. Soc.* **2016**, *138*, 9327–9340. [CrossRef]
42. Lebrero, R.; López, J.C.; Lehtinen, I.; Pérez, R.; Quijano, G.; Muñoz, R. Exploring the Potential of Fungi for Methane Abatement: Performance Evaluation of a Fungal-Bacterial Biofilter. *Chemosphere* **2016**, *144*, 97–106. [CrossRef]
43. Scheutz, C.; Kjeldsen, P.; Bogner, J.E.; de Visscher, A.; Gebert, J.; Hilger, H.A.; Huber-Humer, M.; Spokas, K. Microbial Methane Oxidation Processes and Technologies for Mitigation of Landfill Gas Emissions. *Waste Manag. Res.* **2009**, *27*, 409–455. [CrossRef]

44. Nikiema, J.; Brzezinski, R.; Heitz, M. Elimination of Methane Generated from Landfills by Biofiltration: A Review. *Rev. Environ. Sci. Biotechnol.* **2007**, *6*, 261–284. [[CrossRef](#)]
45. Limbri, H.; Gunawan, C.; Thomas, T.; Smith, A.; Scott, J.; Rosche, B. Coal-Packed Methane Biofilter for Mitigation of Green House Gas Emissions from Coal Mine Ventilation Air. *PLoS ONE* **2014**, *9*, e94641. [[CrossRef](#)]
46. Nikiema, J.; Heitz, M. The Use of Inorganic Packing Materials during Methane Biofiltration. *Int. J. Chem. Eng.* **2010**, *2010*, 573149. [[CrossRef](#)]
47. Melse, R.W.; van der Werf, A.W. Biofiltration for Mitigation of Methane Emission from Animal Husbandry. *Environ. Sci. Technol.* **2005**, *39*, 5460–5468. [[CrossRef](#)]
48. Prenafeta-Boldú, F.X.; Illa, J.; van Groenestijn, J.W.; Flotats, X. Influence of Synthetic Packing Materials on the Gas Dispersion and Biodegradation Kinetics in Fungal Air Biofilters. *Appl. Microbiol. Biotechnol.* **2008**, *79*, 319–327. [[CrossRef](#)]
49. Chanton, J.P.; Powelson, D.K.; Green, R.B. Methane Oxidation in Landfill Cover Soils, Is a 10% Default Value Reasonable? *J. Env. Qual.* **2009**, *38*, 654–663. [[CrossRef](#)] [[PubMed](#)]
50. He, Q.; Wang, J.; Hilliard, M. Culture Systems and Methods of Using Same. U.S. Patent No. 11,339,360, 24 May 2022.
51. Morales, M.; Bonnefond, H.; Bernard, O. Rotating Algal Biofilm versus Planktonic Cultivation: LCA Perspective. *J. Clean. Prod.* **2020**, *257*, 120547. [[CrossRef](#)]
52. Wang, J.; Liu, W.; Liu, T. Biofilm Based Attached Cultivation Technology for Microalgal Biorefineries—A Review. *Bioresour. Technol.* **2017**, *244*, 1245–1253. [[CrossRef](#)] [[PubMed](#)]
53. Gross, M.; Mascarenhas, V.; Wen, Z. Evaluating Algal Growth Performance and Water Use Efficiency of Pilot-scale Revolving Algal Biofilm (RAB) Culture Systems. *Biotechnol. Bioeng.* **2015**, *112*, 2040–2050. [[CrossRef](#)] [[PubMed](#)]
54. Gross, M.; Wen, Z. Yearlong Evaluation of Performance and Durability of a Pilot-Scale Revolving Algal Biofilm (RAB) Cultivation System. *Bioresour. Technol.* **2014**, *171*, 50–58. [[CrossRef](#)]
55. Gross, M.; Henry, W.; Michael, C.; Wen, Z. Development of a Rotating Algal Biofilm Growth System for Attached Microalgae Growth with in Situ Biomass Harvest. *Bioresour. Technol.* **2013**, *150*, 195–201. [[CrossRef](#)]
56. Zhou, X.; Xu, Y. Solar Updraft Tower Power Generation. *Sol. Energy* **2016**, *128*, 95–125. [[CrossRef](#)]
57. Schlaich, J.R.; Bergemann, R.; Schiel, W.; Weinrebe, G. Design of Commercial Solar Updraft Tower Systems—Utilization of Solar Induced Convective Flows for Power Generation. *J. Sol. Energy Eng.* **2005**, *127*, 117–124. [[CrossRef](#)]
58. Ming, T.; Davies, P.; Liu, W.; Caillol, S. Removal of Non-CO<sub>2</sub> Greenhouse Gases by Large-Scale Atmospheric Solar Photocatalysis. *Prog. Energy Combust. Sci.* **2017**, *60*, 68–96.
59. Ming, T.; Caillol, S.; Liu, W. Fighting Global Warming by GHG Removal: Destroying CFCs and HCFCs in Solar-Wind Power Plant Hybrids Producing Renewable Energy with No-Intermittency. *Int. J. Greenh. Gas Control* **2016**, *49*, 449–472.
60. Terlouw, T.; Bauer, C.; Rosa, L.; Mazzotti, M. Life Cycle Assessment of Carbon Dioxide Removal Technologies: A Critical Review. *Energy Environ. Sci.* **2021**, *14*, 1701–1721. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.