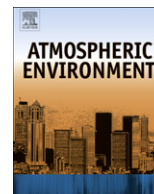




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New Directions: Atmospheric methane removal as a way to mitigate climate change?

Air capture of carbon dioxide (CO₂) has been proposed as a solution to climate change. Various research groups across the world are working on prototypes (e.g., Jones, 2009). The grand challenge is to scale up such prototypes and turn them into cost-effective solutions despite substantial energy requirements. Surprisingly, and notwithstanding the growing implementation of methane capture technologies in the mining industry and methane recovery in landfills, air capture of methane (CH₄) has not received the same attention as air capture of CO₂. This article aims to discuss the advantages and disadvantages of artificial methane removal from the atmosphere or surface waters.

Methane is the second most important anthropogenic greenhouse gas. Its atmospheric concentration has increased from 715 ppbv in the pre-industrial epoch to 1774 ppbv at present as a consequence of human activity. Thus, a reduction to pre-industrial levels would alleviate a radiative forcing of 0.48 W m⁻² amounting to roughly one third of the radiative forcing by CO₂ (Forster et al., 2007). Hypothetically, even larger reductions in radiative forcing could be achieved if methane concentrations were to be reduced below pre-industrial levels. This is conceivable because, unlike CO₂, atmospheric methane does not fertilise ecosystems.

While there are industrial and domestic sources of methane for which emission reductions should be pursued, a significant fraction of the sources are thinly distributed or relate to essential human activities such as agriculture, which makes emission reduction at the source point difficult. Moreover, there is a risk that natural sources of methane increase in a warmer climate through climate feedbacks involving wetlands and melting permafrost. If such feedbacks turn out to be strong, natural emissions of methane could go up significantly and wipe out emissions reductions from anthropogenic sources. In that case air removal could be the only solution to limit methane atmospheric concentrations.

Atmospheric methane concentrations are currently about 0.5% that of carbon dioxide making methane a more elusive target. However, the methane radiative efficiency is one order of magnitude larger than that of carbon dioxide (3.7·10⁻⁴ versus 1.548·10⁻⁵ W m⁻² ppbv⁻¹ – Ramaswamy et al., 2001). Accounting for the relatively short lifetime of methane in the atmosphere, and using Global Warming Potential (GWP) as a basis for CO₂ equivalence, methane is 25 times more potent than carbon dioxide on a per unit mass basis (25*(16/44) = 9.1 more potent on a per volume basis). It has recently been suggested that the methane GWP should be enhanced by approximately one third to 33 because of its indirect effect on sulphate aerosols (Shindell et al., 2009). Consequently, in a putative future climate treaty that rewards atmospheric removal of greenhouse gases and uses a CO₂ equivalence metric, atmospheric methane removal would

still be financially competitive even at a cost of 25 times (or more) the marginal abatement cost of CO₂.

The relatively short methane lifetime can be seen as an advantage (because one gets a fast response to reduction emissions or increased sinks) or a disadvantage (because the response does not last for very long). Fig. 1 shows the temperature change expected from removing 1 kg of methane with and without the removal of the CO₂ that would be emitted during the methane oxidation process (the methodology is described in: Boucher et al., 2009). Most of the climate benefit of withdrawing methane from the atmosphere is realised within 60 years of methane capture, but there is a net climate benefit for as long as 500 years even if the CO₂ stemming from methane oxidation is not captured.

The minimum energy required to separate two gases is given by the opposite of the change in Gibbs free energy when the two gases are mixed. For an atmospheric trace gas such as carbon dioxide or methane, it can be approximated by

$$\Delta Q = (RT/M)(1 + \ln(1/x)) \quad (1)$$

where R is the universal gas constant, T is the temperature, M is the molecular mass of the gas and x is the volume mixing ratio of the gas ($x \ll 1$). Therefore, the minimum thermodynamic energy to separate 1 kg of CH₄ from the ambient air is 2.2 MJ (equivalent to 35.2 kJ mol⁻¹). This is less than 5 times the minimum thermodynamic energy required to separate 1 kg of CO₂ (0.49 MJ). In practice the energy required to separate methane is likely to be much larger than the minimal thermodynamic energy and it is probably technologically more difficult to separate methane than CO₂. However, methane carries significant amounts of chemical energy. The standard enthalpy ΔH^0 for methane combustion is -55.6 MJ kg⁻¹ (CH₄ + 2O₂ ⇒ CO₂ + 2H₂O, $\Delta H^0 = -890.4$ kJ mol⁻¹). Carbon dioxide, since it is fully oxidized, essentially carries no exploitable energy. By exploiting the energy of methane some of the energetic cost of air capture can be recovered. It is noteworthy that methane can burn as soon as enrichment surpasses 5% per volume, thus decreasing the required energy for methane separation by 28% according to Eq. (1).

It is not the purpose of the article to promote a particular technology for methane removal. Nevertheless we propose that technologies suitable for methane air capture should be carefully assessed against their energetic cost and scalability. Existing technologies include cryogenic separation, molecular sieves or gates, and adsorption filters based on zeolite minerals although none of these appear to be currently economically or energetically suitable to be applied to air capture of methane on a large scale.

Moreover it should be noted that it would be almost as beneficial from a climate perspective to oxidise or destroy the methane

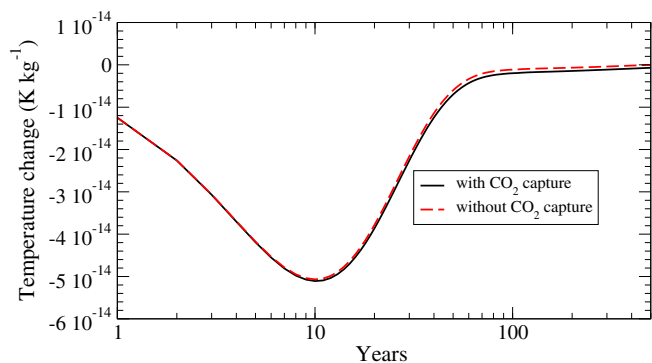


Fig. 1. Temperature change due to an instantaneous air capture of 1 kg of methane (black solid curve). The red dashed curve assumes all the methane is converted to atmospheric carbon dioxide. We assume here that natural sinks of methane in the atmosphere and soils convert 61% of atmospheric methane into atmospheric CO₂ and that artificial oxidation of methane without CO₂ capture would increase this fraction to 100%. (For interpretation of colour in this figure, please refer to the web version of this article.)

in-situ as to capture it (see Fig. 1). This offers an extended range of possible technologies such as conventional precious metal-based catalysts, enzymatic systems, methanotrophic bacteria hosted in bioreactors, and aqueous-phase bio-inspired catalytic oxidation with methanol as a by-product (Sorokin et al., 2008). The potential for these technologies to work at ambient methane concentrations and temperature needs to be assessed.

It is difficult to assess the energetic cost of atmospheric methane removal without considering a particular technique. However, some simple considerations can be made if a chemical technique is used. Although oxidation of methane is an exothermic reaction, the activation energy necessary to break the first C–H bond to start the oxidising chain is large (greater than 400 kJ mol⁻¹). A green chemistry approach would seek to convert gas-phase or aqueous-phase CH₄ ($\Delta_f H_{\text{gas}}^0 \sim -75$ kJ mol⁻¹) into a soluble species such as formaldehyde ($\Delta_f H_{\text{gas}}^0 \sim -110$ kJ mol⁻¹) or formic acid ($\Delta_f H_{\text{gas}}^0 \sim -380$ kJ mol⁻¹) which can then be concentrated at little energetic cost. Formaldehyde and formic acid in solution can be used as feedstock, with hydrogen as one possible product. Recent studies have demonstrated the technical feasibility and efficiency of hydrogen production from formic acid (e.g., Kiliç et al., 2009; Loges et al., 2008). Hydrogen for fuel cells can also be obtained from formaldehyde (Preti et al., 2009). The enthalpy of combustion for hydrogen is -286 kJ mol⁻¹ (i.e., 17.8 MJ kg⁻¹ CH₄), which provides a benchmark for the desirable energetic cost of the first oxidation step which may be achieved at lower activation energies with an appropriate catalyst. A platinum-based catalyst reduces the hydrogen activation energy to less than 1 eV molecule⁻¹ (<95 kJ mol⁻¹). Even more efficient transition metal catalysts are available reducing the activation energy to 50 kJ mol⁻¹ (e.g., Anderson and Maloney, 1988) leaving an estimated 200 kJ mol⁻¹ energy surplus.

In addition to the purely reaction kinetic energies any methane air capture technology will incur processing energy costs. While processing energies for methane air capture cannot be assessed currently a comparison with CO₂ air capture can be made for which detailed energy calculations have been published (c.f. Zeman, 2007 and references therein). Table 1 presents a summary of the energy balance for CO₂ air capture which is used as a guide to assess the energy balance of a potential methane air capture process.

Zeman (2007) provides a detailed energy balance for a specific implementation of CO₂ air capture and a brief comparison with

Table 1
Energy balance for CO₂ and CH₄ air capture.

Item	CO ₂	CH ₄	CH ₄
Energy required	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹ CO ₂ eq) ^a
Air contacting	12–88 ^b	2600–19,000 ^c	285–2088
Other	354–667 ^b	50–400 ^d	6–44
Total	442–679	2650–19,400	291–2132
Energy available	(kJ mol ⁻¹)	(kJ mol ⁻¹)	
Heat	-105 to 0 ^b	-305 to -35 ^e	
Chemical	0	-890 ^f to -286 ^g	
Total	-105 to 0	-890 to -321 ^h	

^a Normalised by the methane 100-year GWP on a molar basis (9.1).

^b From Zeman (2007).

^c Simply estimated by scaling the cost for CO₂ with the ratio of atmospheric concentrations (see text).

^d Methane activation energy (with and without catalyst).

^e Estimated from the standard enthalpy of formaldehyde and formic acid, respectively.

^f Standard enthalpy of combustion of methane.

^g Standard enthalpy of combustion of hydrogen.

^h Maximum process enthalpy.

previous studies. In his work the energy costs for “air contacting”, i.e., sustaining the air flow through the system, are estimated between 12 and 88 kJ mol⁻¹ CO₂. Assuming the energy cost is inversely proportional to the atmospheric concentration and taking into account the lower methane concentration in air (1.76 ppmv versus 380 ppmv of CO₂) the processing energy costs would be 216 times larger for methane than for CO₂. From Table 1 it then becomes clear that this term could dominate energy costs for methane air capture because of the substantially smaller mixing ratio of methane in air. It is obvious that viability of methane air capture will depend on what technical solutions can be found to minimise these energy costs. At the extreme, it is conceivable that the air contacting energy can be provided entirely by renewable energy sources. While there remain several formidable problems the process of methane air capture as one possible climate mitigation option does not appear entirely infeasible.

In conclusion, the goal of methane capture or removal would be to increase the methane sink to balance the increased sources or ultimately surpass them and reduce methane levels in the atmosphere. Secondary benefits are 1) reduced tropospheric ozone production, 2) decreased stratospheric forcing through methane-derived water vapour (predominantly in the stratosphere), 3) energy recycling by exploiting the methane chemical energy, and 4) a possible further reduction in atmospheric CO₂ (through CO₂ capture and storage in the methane oxidation process). We have argued here that there are good physical reasons to consider methane air capture in addition to greenhouse gas emission reductions and carbon dioxide air capture as part of a portfolio approach to mitigate climate change. There are however inherent difficulties associated with the very small concentration of methane in the atmosphere and its low chemical reactivity at ambient conditions but it is possible that these can be overcome. Although we appreciate that the layout of ideas in this article is speculative, it is our hope that it will trigger more policy interest and scientific research on the technology, energetic cost, scalability and cost-effectiveness of air capture of methane.

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