

Thermodynamic evaluation of a conceptual framework for methane mitigation

Master Thesis

Energy Science

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Abstract

In light of the Paris Agreement, the significance of deploying net-negative emission technologies has emerged. However, the scale at which these technologies are predicted to be rolled out is thought to be extremely optimistic, and deeper emissions reductions are needed if the target is to be achieved. Methane is a potent greenhouse gas, therefore a conceptual framework consisting of methane capture and combustion pathways is constructed and effectiveness cross-compared. A thermodynamic approach is employed to assess the exergy required by the process and capacity for avoided emissions. By the direct capture and storage of methane from a coal mine ventilation air emissions source, the exergy required is determined to be 376.73 kJ/kgCO₂ equivalent of avoided emissions. Furthermore, emissions from the power source driving the process is account for and the overall emissions for this pathway amounts to 131 kgCO₂ equivalent emitted per ton avoided. These values are moderately high compared to current values for CO₂ capture thus future optimizing the process for minimum work while is crucial for its successful implementation.

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LIST OF ABBREVIATIONS

| | |
|--------------------|---|
| AR5 | IPCC Assessment Report 5 |
| BECCS | Bioenergy with carbon capture and storage |
| CCS | Carbon capture and storage |
| CEM | Cement plant flue gas |
| CF | Concentration factor |
| CH ₄ | Methane |
| CO ₂ | Carbon dioxide |
| CO ₂ eq | Carbon dioxide equivalent |
| DAC | Direct air capture |
| DACCS | Direct air carbon capture and storage |
| GHG | Greenhouse gas |
| GHGI | Greenhouse gas inventory |
| GtCO ₂ | Gigaton carbon dioxide |
| GWP | Global warming potential |
| H ₂ O | Water |
| IAMs | Integrated assessment models |
| kg | kilogram |
| kJ | kilojoule |
| kmol | kilomole |
| kW | kilowatt |
| kWh | kilowatt hour |
| MJ | Megajoule |
| mol | Mole |
| MWh | Megawatt hour |
| N ₂ | Nitrogen |
| NET | Negative emission technology |
| NO ₂ | Nitrogen dioxide |
| O ₂ | Oxygen |
| ppb | parts per billion |
| RCPs | Representative concentration pathways |
| SO ₂ | Sulfur dioxide |
| Tg | Tera gram |
| USC | Ultra supercritical coal |
| VAM | Ventilation air methane |

1. Introduction

1.1 Background

Since the Paris Agreement from the United Nations Convention on Climate Change was put into effect in 2016, international commitments to mitigating climate change has accelerated (United Nations, 2015). A key element of this agreement addresses further limiting the global temperature increase to 1.5 °C as opposed to the predefined 2 °C. This will require the drastic decrease of current global of greenhouse gas (GHG) emissions. Approximately 1,200 emission pathways to 2100 have been assessed by integrated assessment models (IAMs) in the IPCC Fifth Assessment Report (AR5), each of which evaluate different models, technology combinations and policy commencement times. The pathways are grouped into four main representative concentration pathways (RCPs), with 166 keeping future CO₂ concentrations within 430–480 ppm (RCP2.6), and thus being the range that yields a high probability of reaching the 2 °C target. Achieving this target implies that global cumulative CO₂ emissions relative to 1870 should not exceed 3650 gigatonnes of CO₂ (GtCO₂), however over half of this figure had already been emitted by 2011 (IPCC, 2014).

In light of this, the importance of deploying net-negative emission technologies (NET) to increase the likelihood of achieving the target has emerged (Clarke, et al. 2014; IPCC, 2014). According to the remaining allowable emissions in the budget, global emissions would be required to peak by 2020, and NETs could permit a later peak. Nearly all scenarios associated with RCP2.6 predict that in order to achieve long term climate stabilization, the removal of GHGs from the atmosphere with NETs is essential (Fuss, et al., 2014; Gasser et al., 2015).

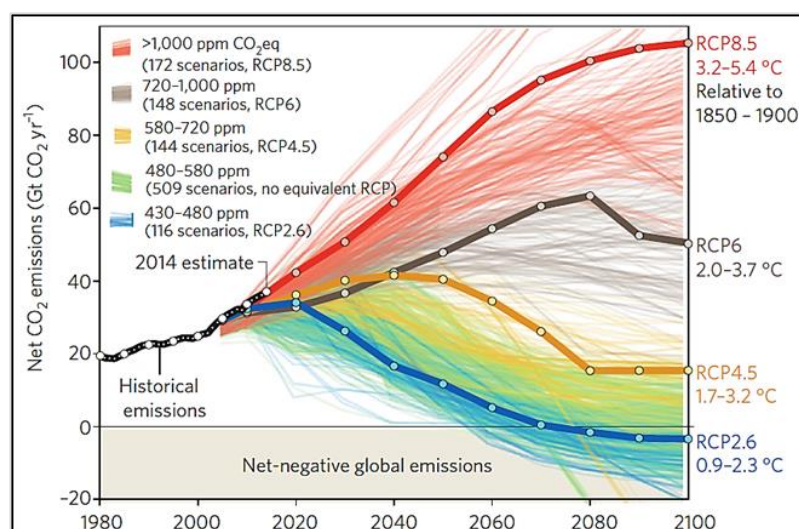


Figure 1. Historical emissions and emission scenarios of AR5. Four RCPs project the average temperature increase in 2081-2100 relative to 1850-1900. (Source: Fuss et al., 2014, Carbon Dioxide Information Analysis Centre, Global Carbon Project, IPCC AR5 database)

Alongside the wide application of carbon capture and storage (CCS) as a CO₂ mitigation technology at point sources, attention has been placed on the potential contribution of a number of alternative NETs. Those of which are most commonly cited and exhibit high potentials as NETs are bioenergy with carbon capture and storage (BECCS), (Pour, Webley, & Cook, 2017; Kemper, 2015), and direct air carbon capture and storage (DACCS) (Goepfert et al., 2012; Sanz-Pérez et al., 2016). However, the massive scale at which they are predicted to be deployed by the IAMs has been noted to be unrealistically optimistic (Larkin et al., 2017; Vaughan & Gough, 2016), and challenges may be presented in the form of the long response time of certain climate system components (Tokarska & Zickfeld, 2015). Furthermore, the potential role of BECCS is constrained by sustainable supply of large scale biomass feedstock or available land (Fajardy, Dowell, & Fajardy, 2017; Smith, et al., 2016). It is evident that NETs have a pivotal role in achieving the target emissions but focus is needed on further developments in NETs to help obtain the deeper emission reductions.

Thus far, the scope for gas separation systems as an NET extend primarily to the capture of CO₂. The different aspects of CO₂ capture systems are thoroughly studied and the literature is extensive. However, strategies involving other GHGs that contribute to climate change have not been studied to the same extent. One such GHG that has been gaining attention is methane (CH₄). Although possessing a shorter life time and present in the atmosphere at low concentrations, it absorbs significantly more energy than CO₂ (IPCC, 2014). Recent literature has implied that the radiative forcing in the climate system due to CH₄ is in fact 20-25% higher than previously reported (Etminan, et al., 2016). Therefore its removal from the atmosphere could prove to be instrumental in decelerating warming temperatures on a shorter time scale.

1.2. Previous studies and problem definition

Current literature indicates that several strategies and components to CH₄ mitigation have been studied. Additionally, sustainable CH₄ oxidation and combustion techniques have been discussed for the mitigation and utilization of ultra-lean CH₄ emissions (Jiang, Mira & Cluff, 2016; Aydin, Karakurt, & Aydiner, 2012). These studies also emphasize the need for increased scientific understanding of non-CO₂ GHG emission mechanisms, such as combustion method, technical feasibility, and engineering applicability. CH₄ separation at ultra-dilute concentrations has been proven to be feasible by a range of adsorption technologies (Olajossy et al., 2003). This strengthens the prospect for CH₄ capture if not from the atmosphere, then it appears to be promising at point sources. Given the urgency in achieving negative emissions to limit the global temperature increase, it is imperative that research efforts are placed not only on CO₂ reductions, but additionally on potential CH₄ reductions. Thus the removal of CH₄ emissions from the source and increasing the CH₄ sink may be a promising approach to mitigating climate change in a shorter time horizon.

Nevertheless, the territory of CH₄ mitigation is not as well studied as CO₂ mitigation. By investigating pathways to CH₄ capture involving various emission sources and capture-combustion scenarios could therefore provide a more comprehensive overview of potential CH₄ capture benefits. Furthermore, the benchmarking of the CH₄ capture system performance, in the same way as CO₂ capture systems, depends on the physical processes driving the technology (Calbry-Muzyka & Edwards, 2014). Therefore the effectiveness of a CH₄ capture pathway can be evaluated based on a thermodynamic approach. This approach then forms the baseline for a high level technology-agnostic analysis.

1.3 Main objective and research question

The underlying motivation of this research is to assess and cross-compare the performance of CO₂ and/or CH₄ strategies, based on fundamental thermodynamic principles. This approach, which is independent of a specific capture technology, is motivated on the one hand by the functionality of offering a general assessment of potential capture systems at CH₄ emission sources, and on the other hand a specific thermodynamic analysis of the work required and emission savings at said emission sources. Taking the above into consideration, the following research question is substantiated:

How do the global warming potential of methane and thermodynamic requirements of its mitigation impact its effective role as a negative emission technology?

Several sub-questions are formulated to assist in answering the main research question:

1. Which emission source opportunities are available for potential CH₄ reductions via gas capture?
2. What are the exergy requirements for the most effective pathway of CO₂ and/or CH₄ removal from the emission source?
3. Taking global warming potentials into account, what are the avoided emissions associated with a given pathway for CO₂/CH₄ mitigation?
4. How do energy provisions contribute to the overall emissions of operating the separation process for a given emission source?

1.4. Scope and boundaries

Multiple aspects of a particular GHG capture solution need to be accounted for in order to meet the challenge of integrating the technology into the current energy system. Aspects including the separation process, and the pathway to separation are interconnected and inherent to the overall system of GHG capture from a particular source. Overall capture performance is dependent on the GHG being captured, from which source, and the subsequent treatment of the GHG. Therefore the separation pathways will examine different GHG capture, combustion, and storage scenarios. The type of storage will not be considered in this research. The performance of the separation pathways is furthermore determined by

the efficiency of the separation process. The primary focus will be placed on the key performance indicators of the separation process and which are explained in detail the method Furthermore, due to the work needed for a separation pathway, the emissions associated with only powering the separation process will be accounted for.

2.Theoretical background

This chapter will outline the scientific and theoretical background upon which the research is based. Firstly, an overview of CH₄ and the concept of the GWP index are discussed in section 2.1. This will be followed by CH₄ mitigation strategies in 2.2. and then an explanation of the fundamental principles behind the thermodynamics of gas separation in section 2.3.

2.1. Methane and the GWP index

2.1.1. Methane sources

Being the second largest GHG contributor to climate change, the potency of CH₄ has made it accountable for approximately 20% of post-industrial global warming (IPCC, 2014). Its atmospheric concentration has accelerated rapidly in the last decade, reaching 1859 parts per billion (ppb) in 2017 (NOAA/ESRL, 2017), and global annual emissions are currently measured to be approximately 560 teragrams (Tg) per year. Around 60% of total CH₄ emission arise from anthropogenic sources and the remaining 40% from natural sources (Saunio, et al., 2016).

Livestock processes, landfills, rice cultivation, and water waste treatment account for just over half of anthropogenic emissions. A third of emissions are thought to originate from fossil fuel activities, and the remaining emissions result from biomass burning and minor industrial processes. CH₄ emissions that originate from natural sources include wetlands, termites, oceans, and methane hydrates.

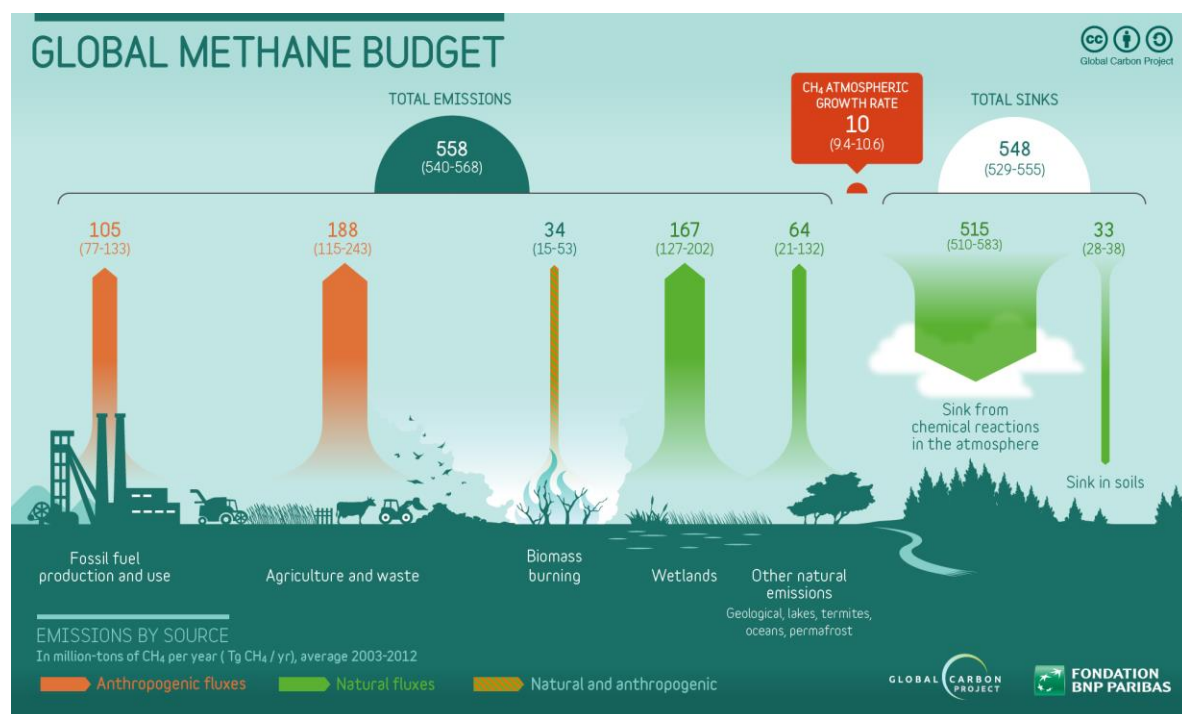


Figure 2. The global CH₄ budget depicting the various CH₄ sources and sinks (Source: Global Carbon Project)

For purposes of this research natural sources are not considered due to scarcity of accurate CH₄ emission data and inter-annual variability in emissions. Although emissions from natural sources contribute significantly, they are difficult to quantifying accurately due to the large distribution of sources, sensitivity to factors such as soil or lake depth resulting in seasonal and annual variability (National Academies of Sciences, 2018).

2.1.2. Global Warming Potential Index

The global warming potential (GWP) of a particular GHG depends on their respective radiative forcing. The radiative forcing provides an effective way of comparing potential relative effect of GHG emissions on the climate. Described in simple terms, it indicates the ability of a forcing agent to affect the energy balance in the atmosphere, and thereby producing a change in stratospheric temperature (IPCC, 2014).

Accordingly, the IPCC AR5 report recently assigned CH₄ with a GWP of 34 (inclusive of climate feedbacks effects), compared to a reference value of 1 given to CO₂. This implies that a unit reduction of 1 ton CH₄, has the equivalent effect of reducing 34 tons of CO₂ from the atmosphere. This GWP value is indicative of the energy absorbed and the relative impact of CH₄ for a 100-year timescale, which is most commonly referred to. However, a GWP value for a GHG's effects on a 20-year timescale is also mentioned. This time scale is more applicable to GHGs with the shorter life times than CO₂, and in the case of CH₄, it is relatively short lived with a lifetime of approximately 12.4 years. This results in a larger GWP value for CH₄ of 86 (Myhre G. , et al., 2013)

2.2 Methane mitigation strategies

Various measures can be taken in either avoiding the release or by capturing CH₄. In terms of gas capture and not specific to CH₄, co-capturing of two gas species could be considered a mitigation option. The combustion of CH₄ has been demonstrated as an approach to CH₄ abatement.

2.2.1. Co-capture of two species

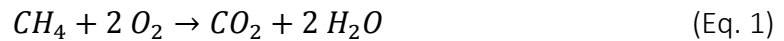
The simultaneous absorption of H₂S and CO₂ has been applied to processes such as natural gas treatment for more than 50 years (Moioli, et al., 2013). The development of satisfactory sorbents for removal of multiple components including SO₂ and NO₂ has been previously studied (Luo, et al., 2018), and is important for this method to progress and extend to the capture of other trace pollutants in the stream.

The numerous pollutants in flue gases are required to be removed in a step-wise manner in separate units, which incurs energy and cost penalties. The application of a combined separation system instead of multi-step system has been demonstrated to be a potential strategy for energy savings if the capture efficiency is satisfactory (Hajari, et al., 2017). Furthermore, if the technical feasibility of simultaneous capture, transportation and

sequestration of two pollutants is further developed it could present opportunities for cost reductions (Tong et al., 2007).

2.2.2. Methane combustion

The combustion of CH₄ has been discussed as a means of its mitigation and/or utilization (ibid). When CH₄ is combusted, it is not a CO₂-free process, as CO₂ is subsequently generated as a product. Assuming complete combustion, the balanced equation is given by,



where one mole of CH₄ requires two moles of oxygen (O₂) to produce one mole of CO₂ and 2 moles of water (H₂O).

With CH₄ being a considerably stronger forcing agent than CO₂ when it comes to its capacity for inducing temperature change (ibid). Its oxidation to CO₂ reduces its climate impact compared to its direct emission to the atmosphere, due to its greater GWP value.

2.3. Principles of minimum thermodynamic work and gas separation

2.3.1. Exergy and minimum work

Exergy can be defined as the amount of useful work available in a reversible process that brings the system to a state of thermodynamic equilibrium (Szargut, 1980). Energy forms possess different abilities in generating work and this can be defined as the energy quality, or exergy. According to the first law of thermodynamics, when a system is changing from state A to state B the difference in total energy of the system is the heat added to the system minus the work done. It suggests that energy is conserved and does not distinguish between energy forms. This can be expressed by,

$$Q - W = \Delta E_{A \rightarrow B} \quad (\text{Eq. 2})$$

where Q is the heat added and W is the work done on the system.

On the other hand, the second law of thermodynamics states that energy quality is destroyed thereby creating a change in energy quality for the different energy forms. A net input of energy quality is required for the energy transformation process in a system to happen. In essence it describes the theoretical minimum work needed to obtain a change in thermodynamic states of the system as the net change in available work (i.e., exergy) of the system. Given that the use of both heat and work may be involved in real world separation of gas mixtures, the minimum work required can be derived from the combination of the first and second laws (Gundersen, 2009; Budzianowski, 2017).

Figure 3 presents a general schematic of a gas separation process including the feed inlet gas A from an emissions source entering a gas separation technology. Stream 1 is a feed mixture inclusive of the targeted component i , stream 2 contains the concentrated target component i after separation, and stream 3 consists of the remainder of stream 1. Depending on the process efficiency, stream 2 is ideally comprised mainly of the target component i in large concentrations and stream 2 should contain very low concentrations of component i . A minimum amount of work, W_{min} , is required to separate the gases and heat, Q_{out} , is released from the system.

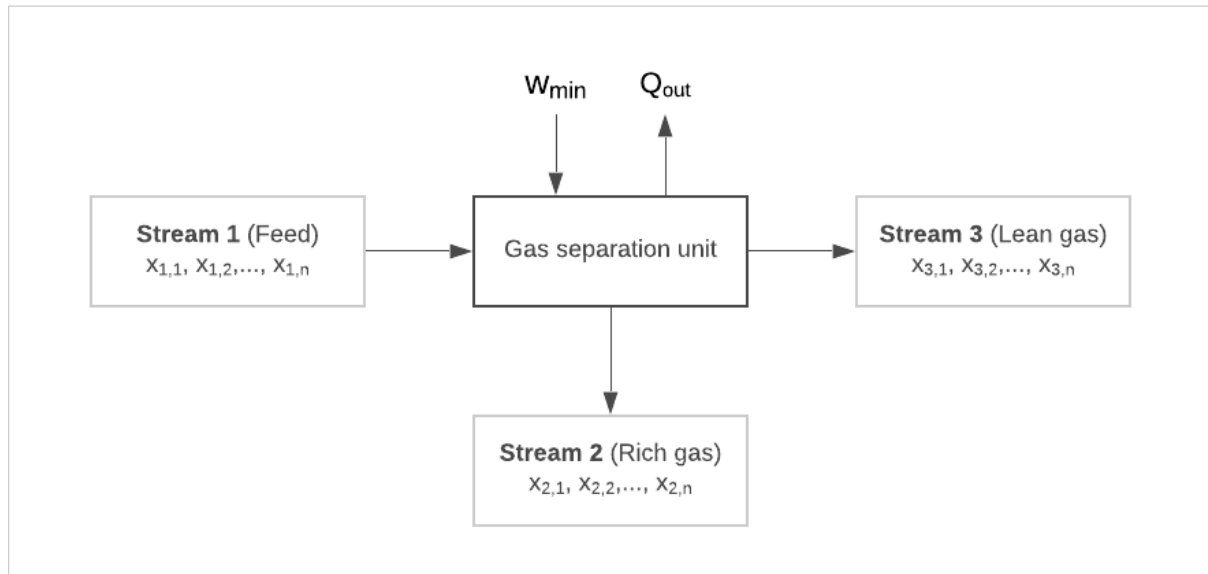


Figure 3. General n-component gas separation process with a feed inlet gas (Stream 1) and two product streams of rich gas (Stream 2) and lean gas (Stream 3). $X_{i,j}$ represents the mole fraction of component j in stream i .

When the system is subjected to a reversible isobaric (constant pressure), isothermal (constant temperature) change, the change in work potential is effectively minimized. Thus the minimum work required is the work potential difference of product and feed streams, which in turn is the difference in exergy of the streams.

$$W_{min} = \Delta\Psi_i \quad (\text{Eq. 3})$$

where W_{min} is the minimum work required and Ψ_i is the exergy of the stream i (House et al., 2011).

For an isobaric and isothermal process, the change in work potential is deduced to the Gibbs free energy. Therefore, the theoretical absolute minimum work required for separation, ΔG_{sep} , is equal to the difference between the Gibbs free energy change of the initial mixed state (stream 1), to that of the separated states (streams 2 and 3),

$$W_{min} = \Delta G_{sep} = \Delta G_2 + \Delta G_3 - \Delta G_1 \quad (\text{Eq. 4})$$

When assuming an ideal gas where the interactions between the gas species are negligible. The partial molar Gibbs free energy for each component j can be denoted by,

$$\frac{\partial G}{\partial n_j} = G_j^o + RT \ln \left(\frac{p_j}{p} \right) \quad (\text{Eq. 5})$$

Where n_j is the partial molar flow rate of j , R is the ideal gas constant, T is the absolute temperature, p_j is the partial pressure of j and p is the total pressure. The total Gibbs free energy G_{tot} of the ideal gas mixture can be expressed by,

$$G_{tot} = \sum_j N_i \frac{\partial G}{\partial N_i} \quad (\text{Eq. 6})$$

Therefore by taking the simple separation process shown in figure 3 as an example, the minimum work required can be written as,

$$W_{min} = -RT \left(N_1 \sum_{j=1..n} x_{1,j} \ln x_{1,j} - N_2 \sum_{j=1..n} x_{2,j} \ln x_{2,j} - N_3 \sum_{j=1..n} x_{3,j} \ln x_{3,j} \right) \quad (\text{Eq. 7})$$

where N_i represents the molar flow rate for stream i , and $X_{i,j}$ is the molar concentration of the component j in stream i . Taking the separation of CO_2 from stream consisting of a gas mixture i as an example, this can be described by,

$$W_{min}^{CO_2} = -RT(x_{CO_2} \ln x_{CO_2} + (1 - x_{CO_2}) \ln(1 - x_{CO_2})) \quad (\text{Eq. 8})$$

When applied to real world operations, separation processes require more than the theoretically defined minimum value. Therefore a second-law efficiency, η , can be applied to compare the actual work required W_{actual} and the ideal performance or the thermodynamic minimum work required, W_{min} (Wilcox, 2012).

$$\eta = \frac{W_{actual}}{W_{min}} \quad (\text{Eq. 9})$$

3. Method

3.1 Qualitative assessment of CH₄ emission sources

Current 'low hanging fruit' opportunities for CH₄ emissions reductions at both anthropogenic and non-anthropogenic sources are explored. This research focuses on the mitigation of CH₄ by means of a gas capture process. Therefore it is important to highlight sectors distinguished by both significant CH₄ emissions and showing most promise for potential mitigation. The emission sources considered for this application are chosen on the basis of certain criteria:

- CH₄ emissions can originate from a point source or distributed source but the source should not be mobile;
- This research requires an a defined inlet gas concentration as an input, therefore specific CH₄ and CO₂ concentrations for the source are required;
- There should be a steady flow of CH₄, i.e., not an intermittent source that shows large variability;
- The level of uncertainty of reported emissions for the source. This will be based on uncertainty ranges reported by the Environmental Protection Agency's (EPA) Greenhouse Gas Inventory (GHGI) (US EPA, 2017).
- There is potential for integration of a gas capture system into the surrounding infrastructure or, evidence of previous successful mitigation efforts via a capture process at the source.

These criteria are set in order to investigate sources where a CH₄ capture system has a relatively greater chance of being implemented, and thus answer sub-question 1. The most viable emission sources will be applied the framework described in the following section and will aid in answering the other sub-questions.

3.2 Conceptual framework for CO₂ and/or CH₄ capture

A conceptual framework for possible capture pathways is introduced, whereby the optimal pathway for CO₂ and CH₄ removal from an emission source via different capture-combustion modes can be assessed. From this framework a thermodynamic analysis can be conducted on the pathways and their capacity for emission reductions can be evaluated.

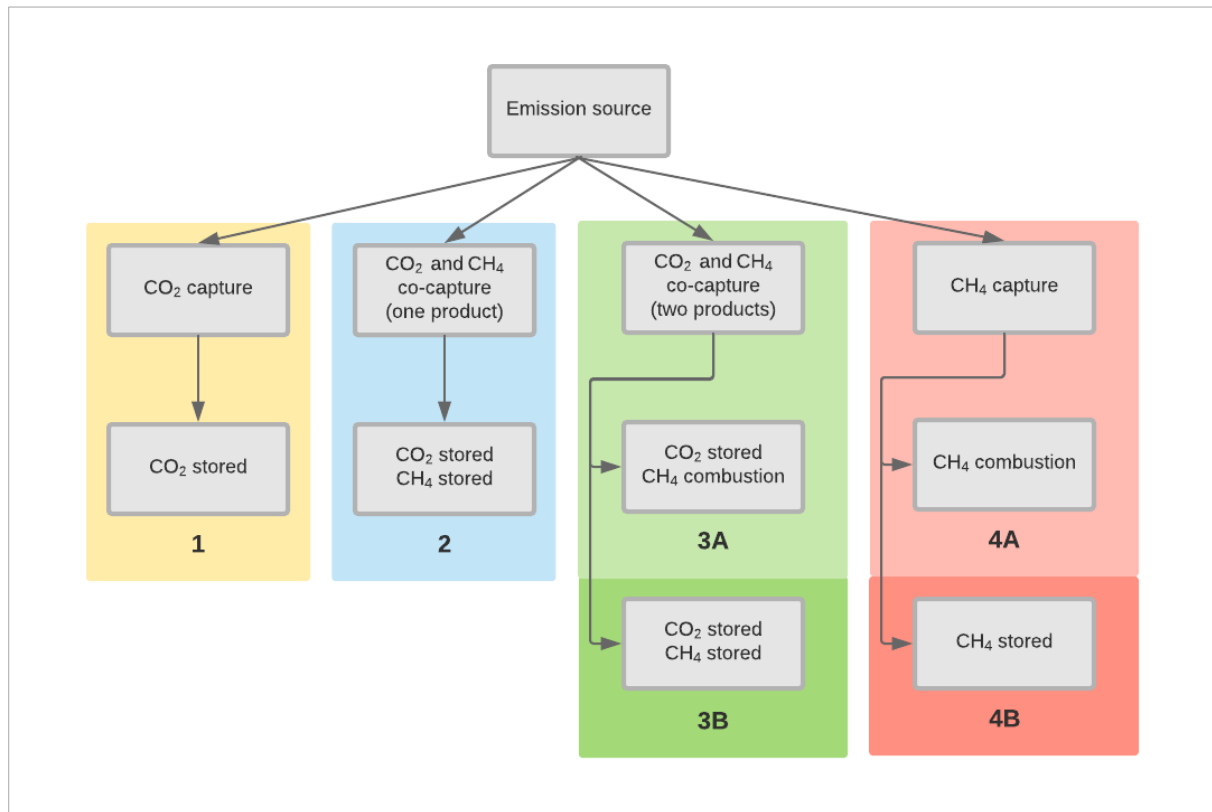


Figure 4. Overview of pathways for CO₂ and CH₄ removal from an emission source. Pathways: 1 (yellow), 2 (blue), 3A (green), 3B (dark green), 4A (red), and 4B (dark red) will be assessed based on key performance indicators.

The overall scheme of the 6 pathways is shown in figure 4. This is followed by more detailed descriptions of the individual capture processes in each pathway in figures 5 to 10. For all the pathways, the streams which focus is placed on are the feed inlet gas entering the gas separation unit, the stream that is emitted (red), and the stream that is stored (blue).

3.2.1. Pathway 1 - CO₂ capture only

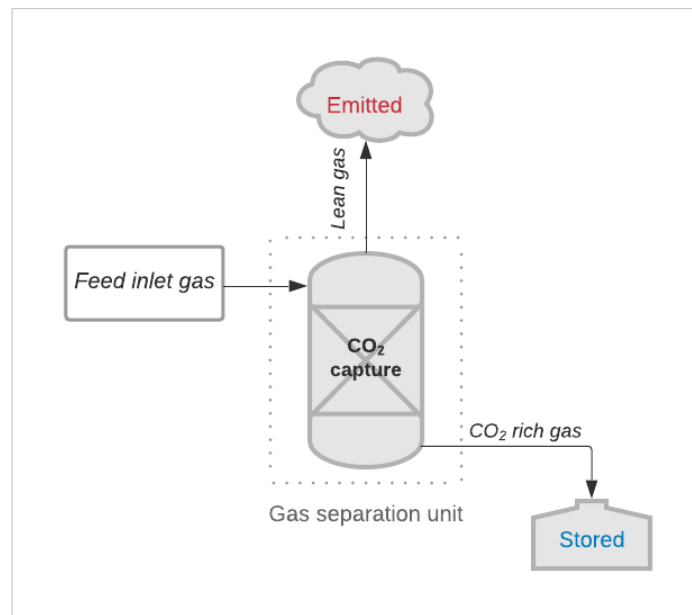


Figure 5. CO₂ capture only with the CO₂ rich gas product stored (blue) and lean gas product emitted (red).

Pathway 1 represents a general CO₂ capture and storage scheme. Only CO₂ is captured from the feed inlet gas and the resulting rich gas is stored, while the lean gas consisting of the remaining components is emitted into air. This is primarily used as a reference pathway to compare against the capture pathways involving CH₄ capture.

3.2.2. Pathway 2 - CO₂ and CH₄ co-capture as one product

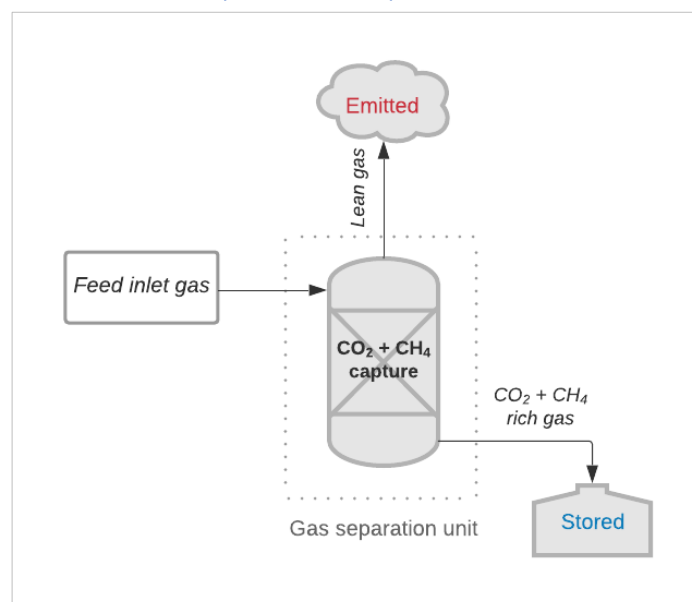


Figure 6. Both CO₂ and CH₄ are co-captured as one product with the rich gas product stored (blue) and the lean gas product emitted (red)

Both CO_2 and CH_4 are directly co-captured from the feed inlet gas. The CO_2 and CH_4 rich gas is stored while the emissions will consist of the remaining lean gas from the separation unit. This pathway is substantiated based on the assumption that CO_2 and CH_4 is captured simultaneously in the same separation process.

3.2.3. Pathway 3A - CO_2 and CH_4 co-capture as two products with combustion

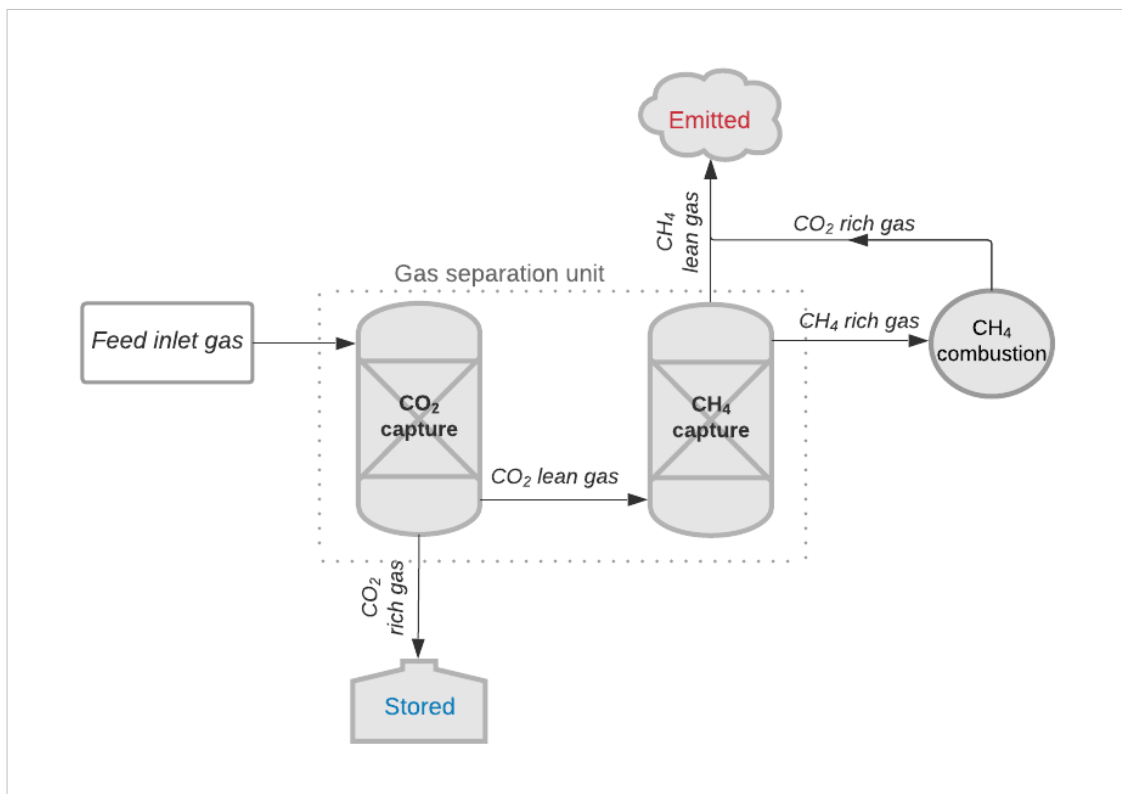


Figure 7. Capture of CO_2 and CH_4 as two products with the CO_2 rich gas stored (blue), the CH_4 rich gas combusted, and the gas remaining from CH_4 capture and combustion emitted (red).

In this pathway CO_2 is firstly captured from the feed inlet gas and stored as the CO_2 rich gas. The CH_4 component is then captured from the remaining gas (CO_2 lean gas). The CH_4 rich gas from this separation process is combusted while the CH_4 lean gas is emitted. According to equation 1, the CH_4 combustion reaction will generate CO_2 which is also emitted. This pathway investigates whether the combustion of CH_4 after capture results in reduced emissions by decreasing the amount of CH_4 emitted and converting it to the less harmful CO_2 .

3.2.4. Pathway 3B - CO₂ and CH₄ co-capture as two products

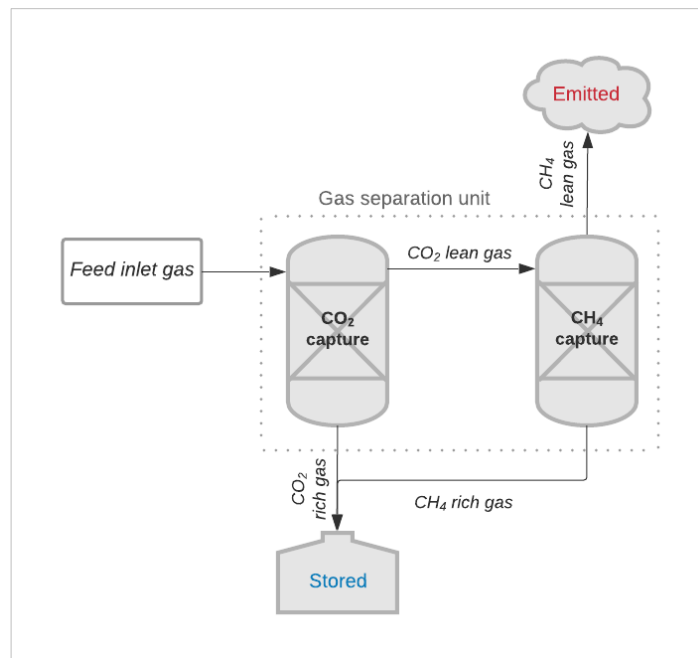


Figure 8. Capture of CO₂ and CH₄ as two products with the rich gas from both CO₂ and CH₄ capture stored (blue), and the lean gas from CH₄ capture emitted (red).

Similar to 3A, pathway 3B involves the initial capture of CO₂ and its storage, with CH₄ being captured from the remaining CO₂ lean gas. After CH₄ capture the CH₄ rich gas is stored, and the remaining lean gas emitted.

3.2.5 Pathway 4A - CH₄ capture only with combustion

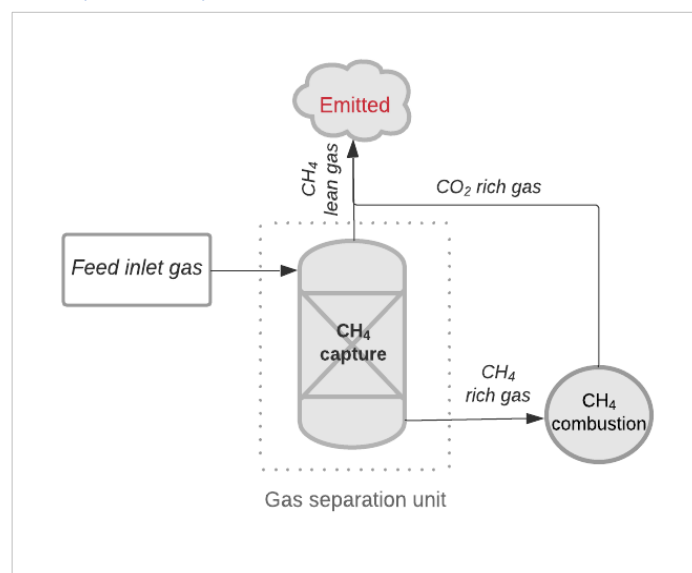


Figure 9. Only CH₄ capture with the CH₄ rich gas combusted, and the gas remaining after CH₄ capture and combustion emitted (red).

Pathway 4A will consider the capture of CH₄ only from the inlet gas. The rich component is then combusted while the lean component is emitted. Analogous to 3A, this pathway will investigate whether combustion of CH₄ and release of the CO₂ product will have an increased mitigating effect through decreased emissions of more harmful GHGs.

3.2.6. Pathway 4B - CH₄ capture only with combustion

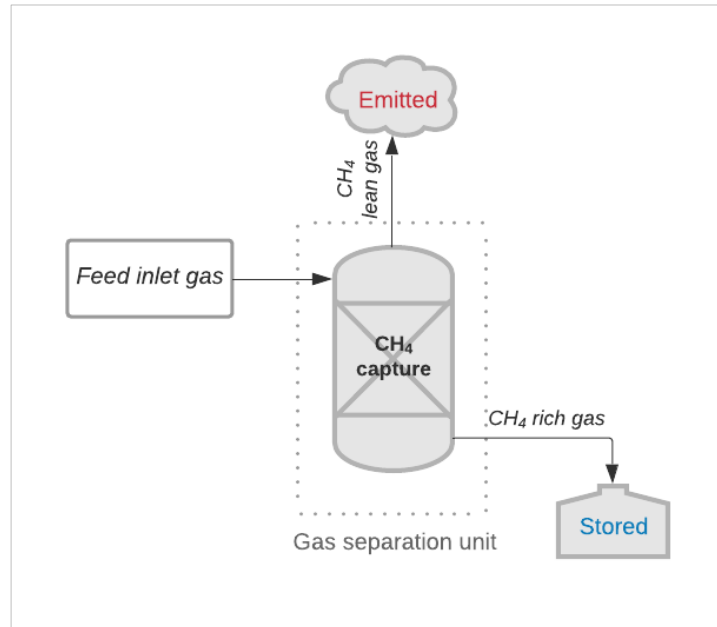


Figure 10. Capture CH₄ only with the CH₄ rich gas stored, and the remaining lean gas after CH₄ capture is emitted (red).

Pathway 4 involves direct capture of CH₄ from an inlet gas and its subsequent storage. The lean gas is then emitted.

These pathways are constructed to observe the mitigation effects of capturing CH₄ and/or CO₂ compared to capturing CO₂ only. Given CH₄'s property as a stronger climate forcer, evidently its capture is advantageous, however it is crucial to examine the exergy required for the separation process in order to assess the overall performance of a particular pathway.

3.3. Thermodynamic work for gas separation

Analyses of the proposed pathways will be carried out with a tool implemented in Matlab[®] (R2017a). Firstly the minimum work is compared to the actual work required for various separation processes in 3.3.1. This will then allow for the computation of key performance indicators in 3.3.2. where the thermodynamic properties for separation and associated emissions for a given pathway are assessed.

3.3.1. Minimum and actual work required for separation

The minimum and actual work required forms the basis for the thermodynamic analysis of the separation pathways. Using eq. 8 the Gibbs theoretical minimum work required for separation of CO₂ from a gas mixture is determined, and likewise for theoretical CH₄ separation. The molar concentration of CO₂ investigated ranges from 0.04%, representative of ultra-dilute concentrations in ambient air, to the higher limit of 20%, which is the average concentration of CO₂ in flue gas from a coal fired power plant. For CH₄ separation the range investigated starts from 0.0002%, which is its concentration in ambient air, to 20%. Values for all the processes are shown in table 1.

According to eq. 9 the second law efficiency describes the ratio of the minimum work (W_{\min}) required to the actual work (W_{actual}) required for CO₂ separation. Values for actual work required for real-world CO₂ separation processes, are shown in table 1. These values include the work required for separation, compression, and transport of the gas for storage.

Table 1. Actual work required to separate CO₂ for real world processes. Molar concentrations are characteristic to the amount of CO₂ in the inlet gas.

| Capture process inlet gas | CO ₂ molar concentration in inlet gas (%) | Actual work required (MJ/kg CO ₂ captured) (W_{actual}) |
|--|--|---|
| Direct air (DAC) | 0.04 | 4.5 |
| Natural gas combined cycle (NGCC) plant flue gas | 4 | 1.2 |
| Ultra-supercritical coal (USC) plant flue gas | 14 | 1 |
| Cement plant flue gas (CEM) | 20 | 1 |

(Sources: Climeworks; Dr. Matteo Gazzani)

The performance ratio between the theoretical minimum work and the actual work for CO₂ separation is determined by applying (Eq. 8). Assuming the same performance ratio, the actual work required for CH₄ separation is determined by multiplying this ratio by the theoretical minimum work for CH₄ separation at the corresponding CH₄ molar concentrations. Linear interpolation is performed to project the actual work required for the range of CH₄ concentrations.

3.3.2. Key performance indicators

To evaluate the effectiveness of a pathway, key performance indicators need to be quantified to help answer sub-questions 2 and 3.

Exergy required for separation

For all of the pathways described in figures 5 to 10, the exergy will be calculated for the separation process that occurs in the gas separation unit. The exergy required for separation was chosen as an important key performance indicator as it is a critical factor in the overall thermal efficiency of the process (Budzianowski, 2017). Furthermore, it will give indication of which energy provisions needed for CO₂-free work to keep the overall emissions low. The exergy (kW) requirement for separation of a component j is calculated by,

$$Exergy_j = W_{j,in} * X_{j,in} * \frac{M_j}{M_{gas,in}} * \dot{m}_{gas,in} \quad (Eq. 10)$$

where $W_{j,in}$ (kJ/kg_j) is the actual work needed for separation, $X_{j,in}$ (kmol_j/kmol_{gas}) is the molar concentration of component j in the inlet gas stream, M_j (kg_j/kmol_j) is the molecular mass of component j , $M_{gas,in}$ (kg_{gas}/kmol_{gas}) is the molecular mass of the inlet gas, and $\dot{m}_{gas,in}$ (kg_{gas}/s) is the inlet gas flow rate.

Using this equation the exergy for separation of the CO₂ and CH₄ components in the inlet gas are calculated, and summed to obtain the total exergy needed for that pathway.

Avoided emissions

As demonstrated in each of the pathways the feed inlet gas enters the gas separation unit and after separation the streams are either stored (i.e. avoided) or emitted. Therefore the general balance for avoided emissions can be shown as,

$$n_{j,avoided} = n_{j,in} - n_{j,emit} \quad (Eq. 11)$$

where n is a unit amount of component j . For this research the unit amount of CO₂eq is defined as the sum of the unit amount of CH₄ equivalent and unit amount of CO₂. The total amount of avoided emissions (kgCO₂eq) is calculated by,

$$\frac{kg_{j,avoided}}{s} = \frac{kg_{j,in}}{s} - \frac{kg_{j,emit}}{s} \quad (Eq. 12)$$

and when,

$$j = CO_2, CH_4$$

it can be calculated that,

$$\frac{kgCO_2eq_{avoided}}{s} = \left(\frac{kgCO_2,in}{s} + \frac{kgCH_4,in}{s} \right) - \left(\frac{kgCO_2,emit}{s} + \frac{kgCH_4,emit}{s} \right) \quad (Eq. 13)$$

Where $kg_{j,in}$ is the kg of component j in the inlet gas and $kg_{j,emit}$ is the kg of component j emitted. The amount of CO_2 ($\frac{kg_{CO_2,in}}{s}$) and CH_4 ($\frac{kg_{CH_4,in}}{s}$) entering from the inlet gas stream can be determined by,

$$\frac{kg_{CO_2,in}}{s} = x_{CO_2,in} * \frac{M_{CO_2}}{M_{gas,in}} * \dot{m}_{gas,in} \quad (\text{Eq. 14})$$

and

$$\frac{kg_{CH_4,in}}{s} = x_{CH_4,in} * \frac{M_{CH_4}}{M_{gas,in}} * \dot{m}_{gas,in} * GWP_{CH_4} \quad (\text{Eq. 15})$$

where GWP_{CH_4} is the global warming potential of CH_4 . Similarly, $kg_{CO_2,emit}$ and $kg_{CH_4,emit}$ can be obtained by,

$$\frac{kg_{CO_2,emit}}{s} = x_{CO_2,out} * \frac{M_{CO_2}}{M_{gas,out}} * \dot{m}_{gas,out} \quad (\text{Eq. 16})$$

and

$$\frac{kg_{CH_4,emit}}{s} = x_{CH_4,out} * \frac{M_{CH_4}}{M_{gas,out}} * \dot{m}_{gas,out} * GWP_{CH_4} \quad (\text{Eq. 17})$$

The above equations can be used to calculate the total amount of avoided CO_2 eq emissions for a given pathway. By dividing eq. 10 by eq. 13, the exergy required per unit of avoided emissions ($\frac{kJ}{kg_{CO_2eq\text{avoided}}}$) is determined by,

$$\text{Exergy required per unit avoided emissions} = \frac{kJ/s}{kg_{CO_2eq\text{avoided}}/s} \quad (\text{Eq. 18})$$

3.3.3. Inlet gas concentration

Concentration factor

As characterized in the framework of pathways, this research investigates the influence of direct or parallel CH_4 mitigation with CO_2 from particular inlet gas stream. A distribution of potential inlet gas CH_4/CO_2 concentrations can give a more comprehensive perspective of how the exergy and emissions deviate accordingly. A concentration factor (CF) is defined to collate the effects of increasing/decreasing CH_4 molar fraction compared to that of CO_2 ,

$$CF = \frac{x_{CH_4}}{x_{CO_2}} \quad (\text{Eq. 19})$$

with x_{CH_4} and x_{CO_2} being a given concentration of CH_4 and CO_2 . The variation in CF will firstly be used to show the trend in the exergy required and emissions for a given pathway, and

following a more specific analysis can be conducted for an inlet gas concentration for particular case study.

Specific case studies

The emission sources considered most adequate from the selection process in section 3.1. can then be applied as an input to Matlab to provide case specific evaluations. The known feed inlet gas composition are entered into the tool constructed in Matlab to simulate the capture processes. Thereby the performance of the pathways for a specific inlet gas composition can be calculated and be cross-compared for the best option in terms of exergy requirement and avoided emissions. The exact input concentrations of CH₄ and CO₂ for the emission sources are defined in the data input tables of the results section.

3.4. Emissions penalty

To achieve overall negative emissions from the system, added emissions produced by the energy provisions are required to be sufficiently balanced by the avoided emissions. This scenario is more likely achievable with CO₂-free power sources, however depending on the amount of work needed, the power from the current electricity generation mix may result in an emissions penalty to the separation pathway.

After determining the most attractive pathway for a specific case study, the emissions intensity of the power source will be accounted for to determine the sources required to maintain overall negative emissions from the system.

4. Results

4.1. Qualitative assessment of CH₄ emission sources

Despite a clear understanding and characterization of CH₄ emission sources, the exact amount of emissions, their respective variability, and feedbacks remain difficult to quantify. It has been expressed that, “*It is clear that some further untangling of CH₄ sources needs to happen*”, (Crill & Thornton, 2017).

Nonetheless, assessments have been conducted at many emission sources in an attempt to quantify the volume, fluctuation, and intensity of CH₄ at the various sites. Table 2 presents major CH₄ sources which had potential for CH₄ capture systems. These sources were particularly notable and selected based on literature research. Furthermore, the recent report from The National Academies of Sciences, Engineering, and Medicine (NASEM) extensively discusses the characterization of anthropogenic CH₄ emissions, and provided a clear overview of current significant CH₄ sources (NASEM, 2018). While EPA’s 2015 Greenhouse Gas Inventory stipulates the uncertainty levels in emission estimates in sources. Using these resources the findings are grouped into source categories and summarized in table 2. It is followed by a detailed discussion of the source categories.

Table 2. Selection criteria results for major CH₄ sources.

| Source category | Selection criteria | | | | |
|--|--|---|-------------------------------------|-------------------------------------|--------------------------------|
| | Type of source | CH ₄ & CO ₂ concentration available | Steady CH ₄ flow | Gas capture integration feasibility | Emission data confidence level |
| Enteric fermentation | Point source but wide spatial coverage | Yes but for specific days and farm circumstances | No, daily and seasonal variability | Possible but limited | Medium |
| Petroleum and natural gas systems | Point source | Yes but measurements taken for surrounding area | Yes but for a wide surrounding area | Limited | Low |
| Landfills | Point source | Yes | Yes | Yes | Medium |
| Coal mining | Point source | Yes | Yes | Yes | High |

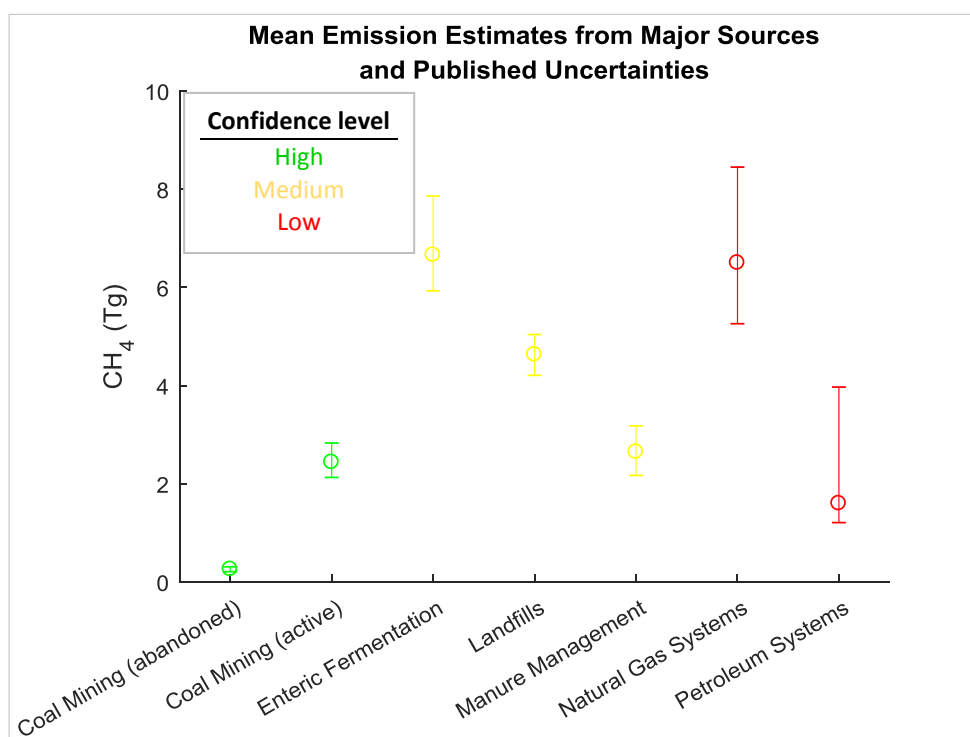


Figure 11. Comparison of uncertainty ranges of CH₄ emission values for a source, as reported by EPA's Greenhouse Gas Inventory. (Source: EPA, 2017; NASEM, 2018)

Based on EPA's Greenhouse Gas inventory, the levels of uncertainty in the emission values are plotted for major sources of CH₄ in figure 11. The confidence levels of emission estimates will aid in the screening for the CH₄ emission source most suitable for this research.

Enteric fermentation, manure management and landfill gas

Although enteric fermentation and manure management are significant contributors to global CH₄, the locations are widely distributed and emissions are relatively disseminated. This implies the implementation a gas capture system in the infrastructure both from a technical and economic perspective would be unfavorable. There is diverse spread of activity data that influence CH₄ emission on cattle farms, which range from barn/farm capacity, species, seasonal variability, all which contribute to varying concentrations and volumes of CH₄. This is reflected in figure 11, where the accuracy of agricultural emissions and landfills are represented by a medium confidence level. Landfill gas has been studied for CH₄ mitigation, however the key uncertainties are site and region specificity of emissions, and dynamic soil and climate effects. For the purposes of this research, specific CH₄ and CO₂ concentrations are limited therefore these sources refrained from consideration (ibid).

Natural gas and petroleum systems

New reports indicating oil and gas industries are responsible for recent increases in global CH₄ (Worden, et al., 2017). Fugitive emissions or unintentional CH₄ releases contribute significantly to the total emissions, however they are hard to quantify and obtain accurate measurements (Hopkins, 2016). As shown in figure 11, natural gas and petroleum systems

exhibit low confidence levels due to temporal variability in emissions, with fluctuations of $\pm 50\%$ noted (EPA, 2017). There exists an abundance of emission sources, either from processing, distribution or transmission operations. Therefore measurements taken are usually for the wide surrounding area, which makes it difficult to obtain specific CO_2 and CH_4 concentration levels.

Coal mining

Mitigation options involving ventilations systems at coal mines are well-studied (ibid). Although CH_4 is present in low concentrations the volume at which the air is emitted is huge and contribute significantly to anthropogenic CH_4 emissions. According to figure 11, coal mining emissions are observed to have the lowest level of uncertainty. The main uncertainty being differences in gas measurements underground than at the surface (EPA, 2017). Nonetheless, emission are noted to be easily quantified as the source is localized and are in the range of 0.3 to 1.5% (Su & Agnew, 2006).

Direct air capture

Direct air capture of CH_4 is seldom discussed. However, DACCS is already noted as a capable and prospective NET (Socolow R. et al, 2011). Since CH_4 and CO_2 concentrations in ambient air are steadily quantified, investigating the capture of CH_4 simultaneously with CO_2 may offer energy savings and perhaps could be retrofitted into existing DACCS systems.

The main obstacle associated with livestock and natural gas/petroleum systems is that emissions vary temporally and spatially, therefore it is difficult to quantify a specific CH_4 or CO_2 concentration, which is key for this research. Landfill gas is well studied but have uncertainties and are site specific. Coal mine ventilation air offers the most prospect as an emission source to investigate in this study due to availability of CH_4 and CO_2 concentrations for the gas, limited variability in concentrations, prior research conducted on site, and low uncertainty levels in volume of emissions. Furthermore capture from ambient air will also be considered for reasons mentioned above.

4.2. Minimum and actual work requirement

The minimum and actual work required is determined as per the methodology stated in section 3.1., and using input values in table 3. Firstly results will be shown for CO_2 then similarly for CH_4 followed by a brief discussion of values obtained.

Table 3. Input values for the inlet gas concentration used in Matlab to determine the exergy requirement

| Inlet gas | Unit | N ₂ | O ₂ | Ar | CO ₂ | CH ₄ | H ₂ O |
|----------------|-------------|----------------|----------------|--------|----------------------|--------------------|------------------|
| Composition | vol % | 0.7808 | 0.2095 | 0.0093 | 400×10^{-6} | 2×10^{-6} | 0 |
| Molecular mass | kg/ kmol | 28.0134 | 31.9988 | 39.948 | 44.0095 | 16.0423 | 18.0153 |

| | | |
|--------------------|------|-----|
| Temperature | K | 298 |
| Pressure | bar | 1 |
| Flow rate | kg/s | 10 |
| Capture efficiency | % | 90 |

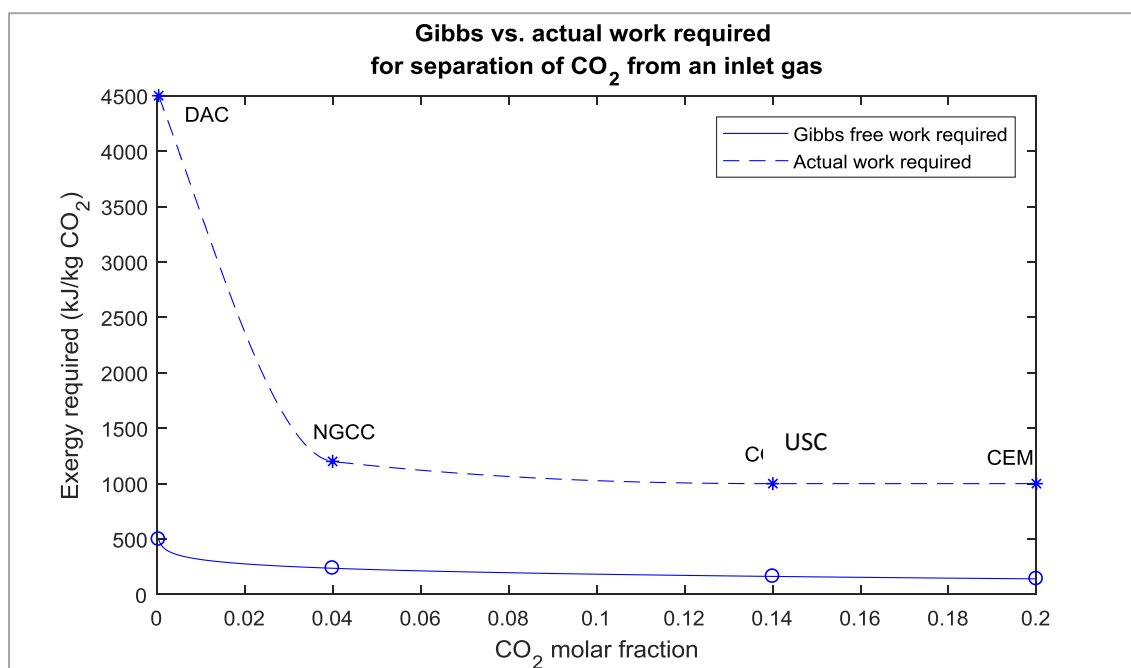


Figure 12. The thermodynamic minimum work per kg CO₂ separated (circle) vs. molar fraction of CO₂, and the actual work required for real world processes (star).

The theoretical minimum work required per kg CO₂ separated for a range of CO₂ concentrations is calculated and values are shown in table 4. In figure 12 the actual work required for separation of a CO₂ concentration in a real world process are indicated (stars), and used to calculate the 2nd law efficiency of the process.

Table 4. Theoretical Gibbs free energy for separation of a CO₂ molar concentration, the actual work required, and the corresponding 2nd Law efficiency

| Separation process | Molar concentration CO ₂ (vol %) | Gibbs Free Work for separation (kJ/kgCO ₂) | Actual work required (kJ/kgCO ₂) | 2 nd Law efficiency (-) |
|--------------------|---|--|--|------------------------------------|
| DAC | 0.0004 | 497 | 4,500 | 9.06 |
| NGCC flue | 0.04 | 236 | 1,200 | 5.07 |
| USC flue | 0.14 | 163 | 1,000 | 6.14 |
| Cement flue | 0.20 | 163 | 1,000 | 6.14 |

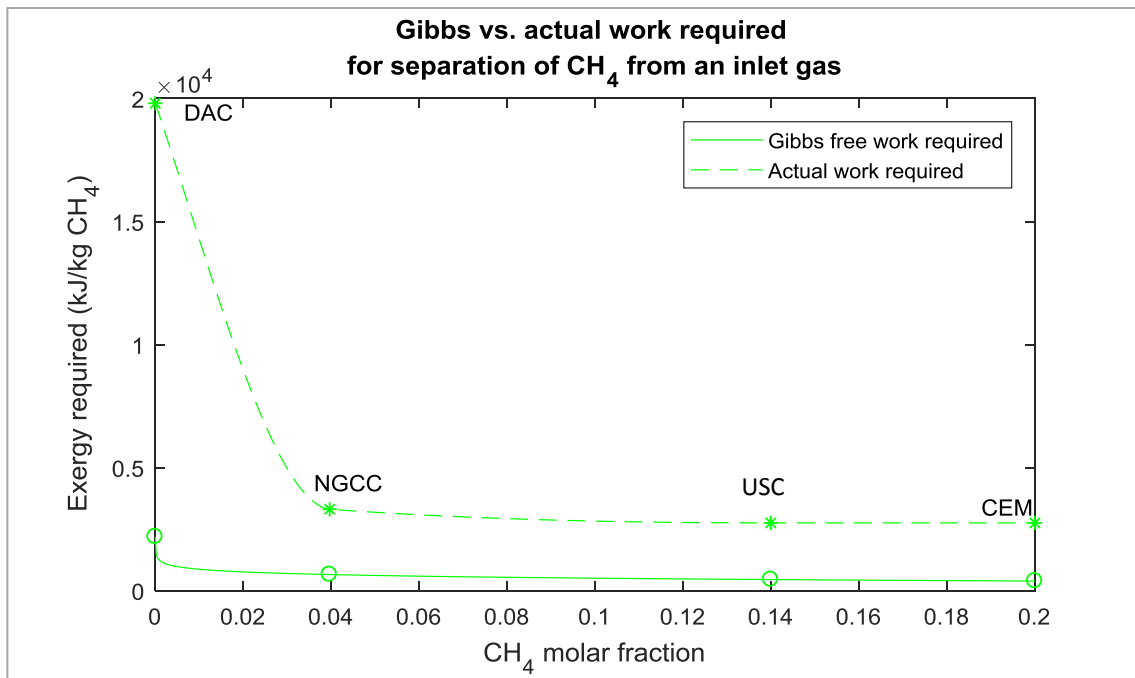


Figure 13. The thermodynamic minimum work per kg CH₄ separated (circle) vs. molar fraction of CH₄, and the actual work required for real world processes (star).

Table 5. Theoretical Gibbs free energy for separation of a CH₄ molar concentration, the actual work required, and the 2nd Law efficiency.

| Separation process | Molar concentration CH ₄ (vol %) | Gibbs Free Work for separation (kJ/kgCH ₄) | Actual work required (kJ/kgCH ₄) | 2 nd Law efficiency (-) (same as for CO ₂ separation) |
|--------------------|---|--|--|---|
| DAC | 2 × 10 ⁻⁶ | 2,187 | 19,806 | 9.06 |
| NGCC flue | 0.04 | 650 | 3,298 | 5.07 |
| USC flue | 0.14 | 448 | 2751 | 6.14 |
| Cement flue | 0.20 | 448 | 2751 | 6.14 |

The theoretical minimum work required per kg CH₄ separated is calculated similarly to that of CO₂. Using the same 2nd law efficiency for CO₂ separation, the actual work required for CH₄ separation is estimated and resulting values are presented in table 5. To obtain the actual work required for the range of CO₂ and CH₄ concentrations linear interpolation is performed for the corresponding molar fractions.

The minimum work follows a logarithmic trend with the CO₂ and CH₄ concentration. Therefore, it is observed that the minimum work required to remove CO₂ from air (0.04 %) at 497 kJ/kgCO₂, is approximately three times greater than the work required to remove CO₂ from a pulverized coal plant flue gas (12%) at 163 kJ/kg. Given that the concentration of CH₄

in air (0.0002%) is much lower than that of CO₂, the amount of work required is estimated to be 2,187 kJ/kg CH₄, which is around four and a half times larger than work needed to capture CH₄ at a concentration of 12%, at 448 kJ/kg. This difference in energy indicates that it would be preferable to capture a component with a larger initial concentration in the inlet gas, and from a point source as opposed to capture from the atmosphere.

4.3. Concentration factor: exergy and emissions avoided

Using a concentration factor as specified by eq. 19, the general trend of exergy required for separation as a function of a given CH₄ and CO₂ ratio is shown for each pathway.

4.3.1. Concentration factor

Figure 14 shows the trend for exergy required per kgCO₂eq in the inlet gas as a function of the concentration factor (CF). For this analysis, the concentrations are defined as $x_{CH_4} = 2$ and $x_{CO_2} = 400$, which is analogous to CH₄ and CO₂ concentrations (ppm) in air. Therefore, the CF for CH₄ and CO₂ in air is initially defined as,

$$CF = 2 / 400 = 0.005$$

x_{CO_2} is kept constant and x_{CH_4} is increased from 2 to 400, so that the CF increases from a value of 0.005 to 1 where,

$$CF = 400 / 400 = 1$$

Therefore the concentration of the inlet gas consists of the CF of CH₄/CO₂ starting from the ratio of CH₄ and CO₂ in air, and CH₄ concentration is increased until the the ratio is 1. This can then be used to show how the exergy required and emissions avoided vary as the CH₄ concentration versus the CO₂ in the feed inlet gas varies.

4.3.2. Exergy required per unit of inlet gas, and avoided emissions

The exergy required per unit of kgCO₂eq in the inlet gas and per unit of kgCO₂eq avoided as a function of the CF is shown for each of the pathways. The effect of the GWP of both 100 years and 20 year time horizons (34 and 86 respectively).

Exergy per inlet gas

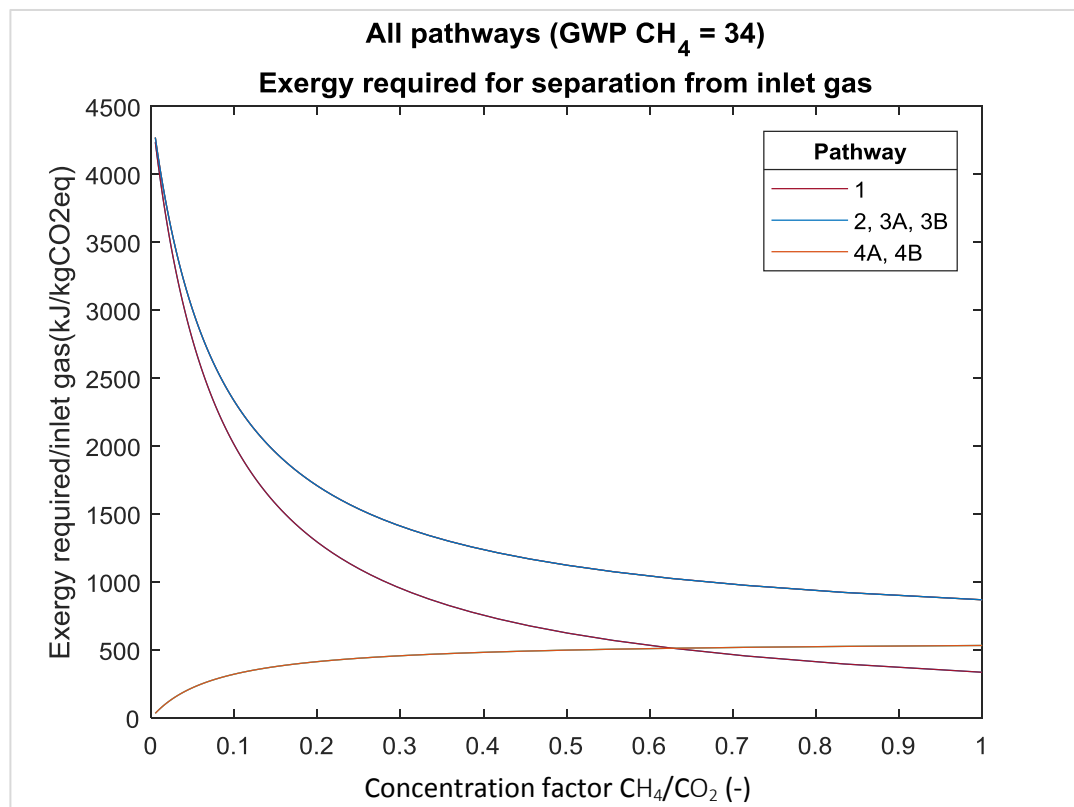


Figure 14. Exergy required for separation per kgCO₂eq from the inlet gas, for a molar fraction of CH₄/CO₂.

Pathway 1

The exergy required starts at 4247 kJ/kg CO₂eq when the CF is low and decreases to 336 kJ/kgCO₂eq as CF approaches 1. Since only CO₂ is captured in this scenario and the concentration of CO₂ is constant in the CF, the exergy required per kgCO₂ in the inlet gas is 4500 kJ/kgCO₂. However this figure shows the exergy unit of kgCO₂eq in the inlet gas which includes kgCH₄. Therefore a decrease is observed as the amount of CH₄ increases in the CF, which represents an increase of kgCH₄ in the inlet gas, and thus decreasing the exergy required per kgCO₂eq in the inlet gas as the CF increases to 1.

Pathway 2, 3A and 3B

These pathways involve the capture of both CO₂ and CH₄, with the same amount of kgCO₂eq entering the separation unit, therefore the trend is the same for these pathways. When CF is small with the CH₄ concentration much lower than that of CO₂, the exergy required is 4271 kJ/kgCO₂eq. CH₄ increasing in the inlet gas results in a decrease in exergy required to 869 kJ/kgCO₂eq as CF goes to 1. Over the range of CF, the exergy required for these pathways is greater than that for pathway 1. Pathway 1 only considers the capture of CO₂ while 2, 3A and 3B also involve capturing CH₄, therefore in addition to the exergy required for CO₂ separation (kJ/kgCO₂), the exergy needed for separation of CH₄ (kJ/kgCH₄) needs to be accounted for.

Pathways 4A and 4B

Both 4A and 4B consider the capture of CH₄ only, thus their trends are similar. As the molar fraction increases and CH₄ concentration matches that of CO₂, the exergy required gradually increases to 533 kJ/kgCO₂eq avoided. The exergy required increases as the CF increases. This is uncharacteristic as the exergy required for CH₄ separation should decrease with increasing CH₄ concentration, as seen in the minimum energy required for separation. A plausible explanation is that the CH₄ concentrations in CF is too low and would have to be higher than CO₂ for 4A and 4B to be exergetically favorable.

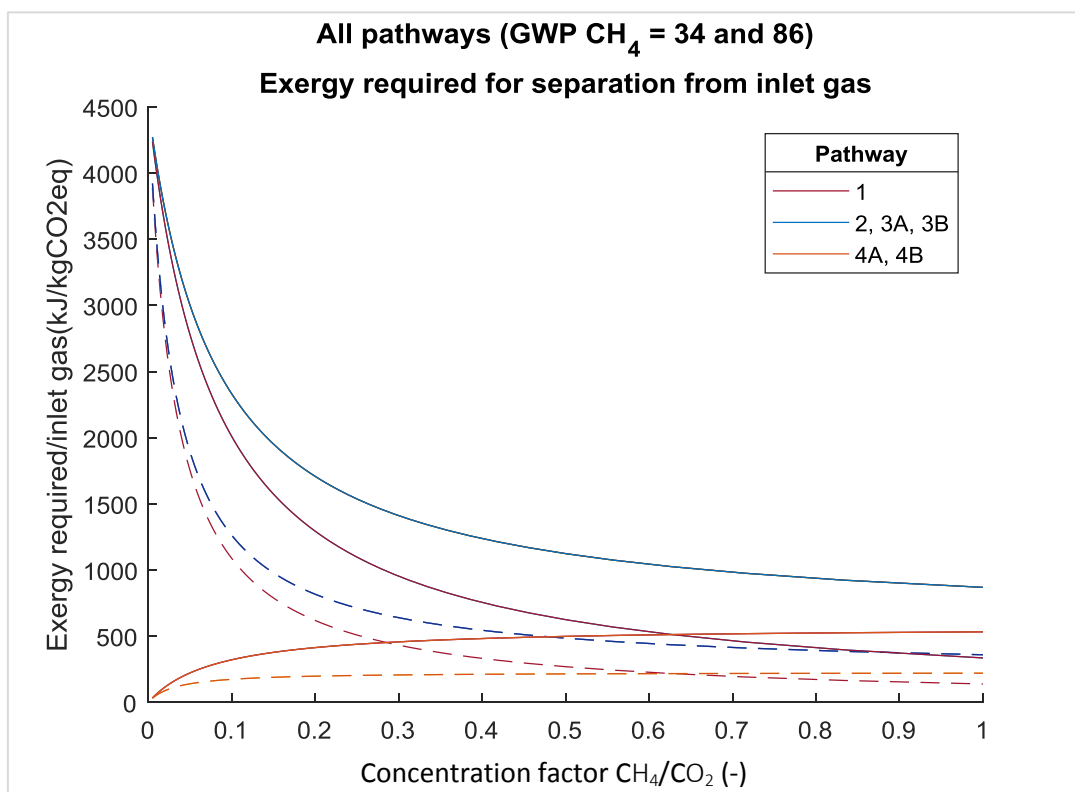


Figure 15. Exergy required for separation per kgCO₂eq from the inlet gas, for a molar fraction of CH₄/CO₂. The solid lines represent the exergy required for a GWP of CH₄ at 34, and the dashed lines for a GWP of CH₄ at 86

Figure 15 demonstrates the effect of increasing the GWP of CH₄ to 86. For all pathways the exergy requirement decreases over the range of the CF. This is expected as the increased GWP influences the kgCH₄ in the inlet gas, therefore increasing the overall kgCO₂eq and decreasing the exergy needed.

Exergy per emissions avoided

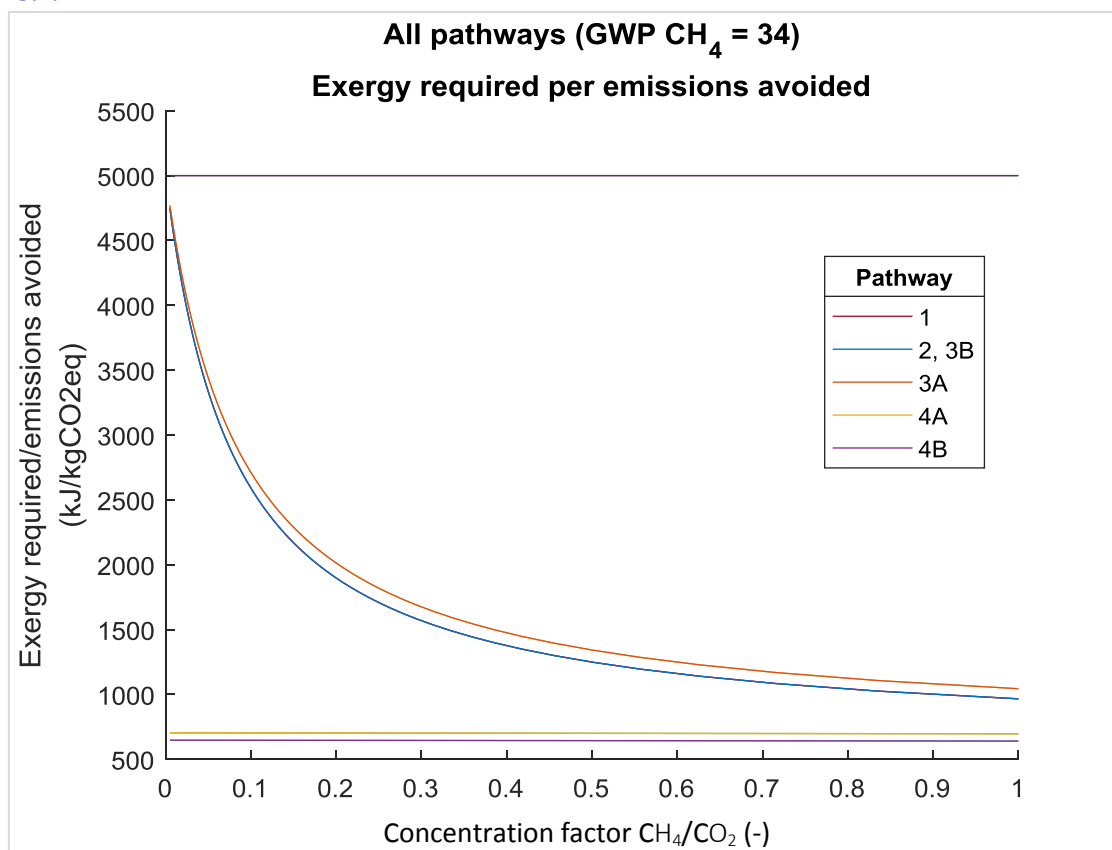


Figure 16. Exergy required for separation per kgCO₂eq avoided, for a molar fraction of CH₄/CO₂.

Pathway 1

As the molar concentration of CO₂ is held constant, the amount of exergy required for separation of CO₂ is therefore constant from 0 to 1 for the CF. The exergy required is 5000 kJ/kgCO₂. This is characteristic as the assumed capture efficiency of the technology is 90% and as discussed in the method, the actual work required for separation of CO₂ from air is at a concentration of 400 ppm is 4500 kJ/kgCO₂.

Pathways 2, and 3B

2 and 3B both involve the capture of CO₂ and CH₄, with the difference being the co-capture of both gases in 2 as one product, and the capture of CO₂ and CH₄ as two products in 3B. In both pathways the captured products are stored. The same value for exergy required is seen for 2 and 3B, with the exergy required decreasing as the amount of CH₄ increases. This is due to the same components being avoided for a given inlet gas concentration. Therefore, the difference in the amount of avoided emissions depends on the capture efficiencies of the individual CO₂, CH₄, and co-capture processes.

Pathway 3A

The trend is similar to 2 and 3B, as both CO₂ and CH₄ is captured, however exergy required is slightly higher. The amount of emissions avoided in 3A is lower than that for 2 and 3B, and can be explained by the added combustion step. The combustion of CH₄ does indeed reduce

kgCO₂eq emissions compared to capturing and storing only CO₂. However it seems that mitigation of CH₄ emissions via storage of the captured product results in slightly more reduced emissions than combustion of CH₄.

Pathways 4A and 4B

The exergy remains constant for 4A and 4B over the range of CF. This is due to the amount of emissions avoided increasing as the exergy required for decreasing.

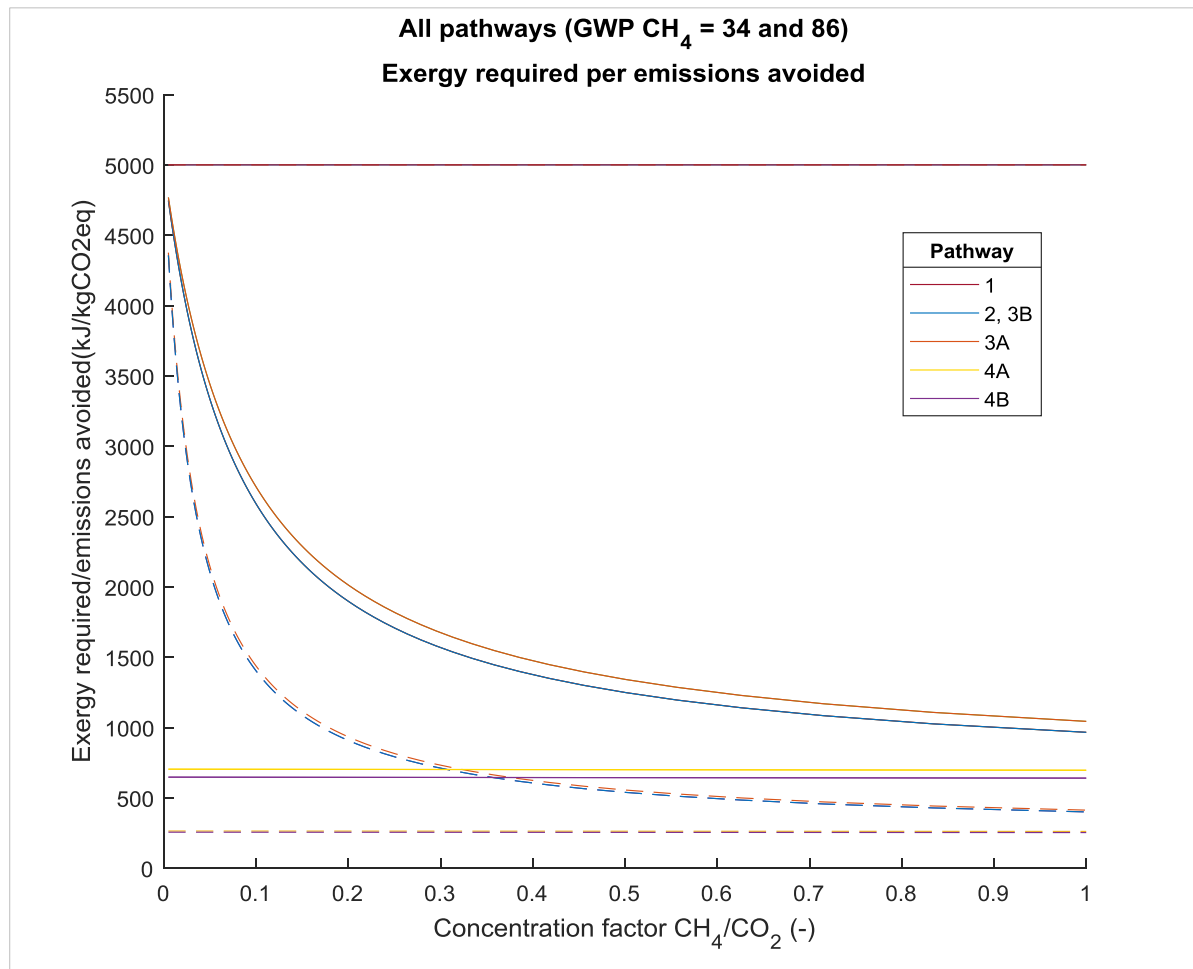


Figure 17. Exergy required for separation per unit of emissions avoided for GWP of CH₄ = 34 and 86, as a function of CF.

The effect of using a GWP value of 86 (dashed lines) is the same as discussed above for the exergy required per inlet gas. As CH₄ increases so does the kgCO₂eq avoided thereby decreasing the exergy required. For pathways 2, 3A, and 3B, it can be observed that when the GWP of CH₄ is 86, the exergy required per emissions avoided becomes less than that for a GWP value of 34 in 4A and 4B when the CF is approximately at 0.3. This further supports that when the concentration of CH₄ becomes higher it becomes increasingly more favorable for capture.

4.3.3. Avoided emissions

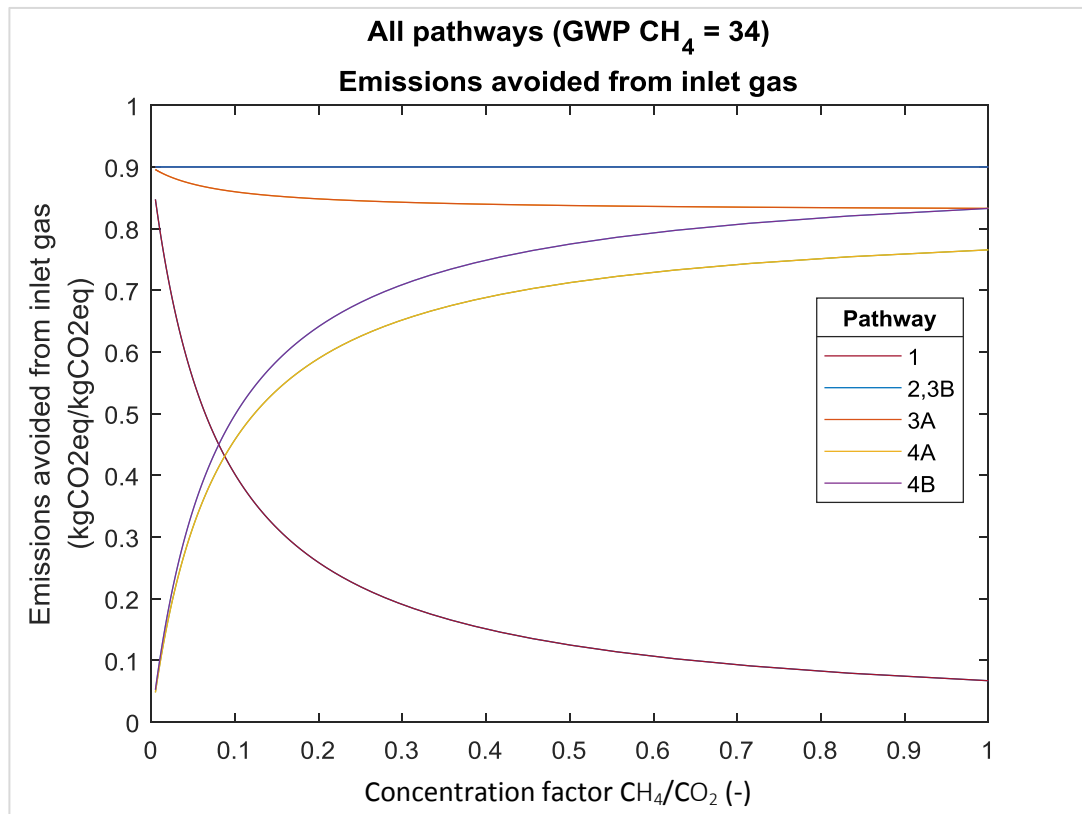


Figure 18. Emissions avoided per inlet gas as a function of CF, for a GWP of $CH_4 = 34$

Pathway 1

When CF is low the amount of emissions avoided are high. As the CH_4 concentration increases the emissions avoided decreases substantially. However, it remains favorable to capture CO_2 , as long as CH_4 concentrations are low.

Pathways 2 and 3B

Similarly to the exergy required (figure 16) and for the same reasons, the amount of emissions avoided for 2 and 3B are equivalent for the range of CF. As discussed, the amount avoided will depend on the capture efficiency for the individual separation processes.

Pathway 3A

The emissions avoided are high for the range of CF, decreasing slightly as the CF increases. It was observed earlier that combustion of CH_4 results in more emissions than the storage of CH_4 , therefore this trend can be attributed to less emissions being avoided as CH_4 concentrations increase.

Pathway 4A

As expected, when CF increases the amount of emissions avoided increases. Capture at a low CF would not be favorable but as the CF increases CH_4 capture becomes more promising.

Pathway 4B

The same trend as 4A is observed. However more emissions are avoided as CF increases, which strengthens the case for CH₄ storage as opposed to combustion after capture.

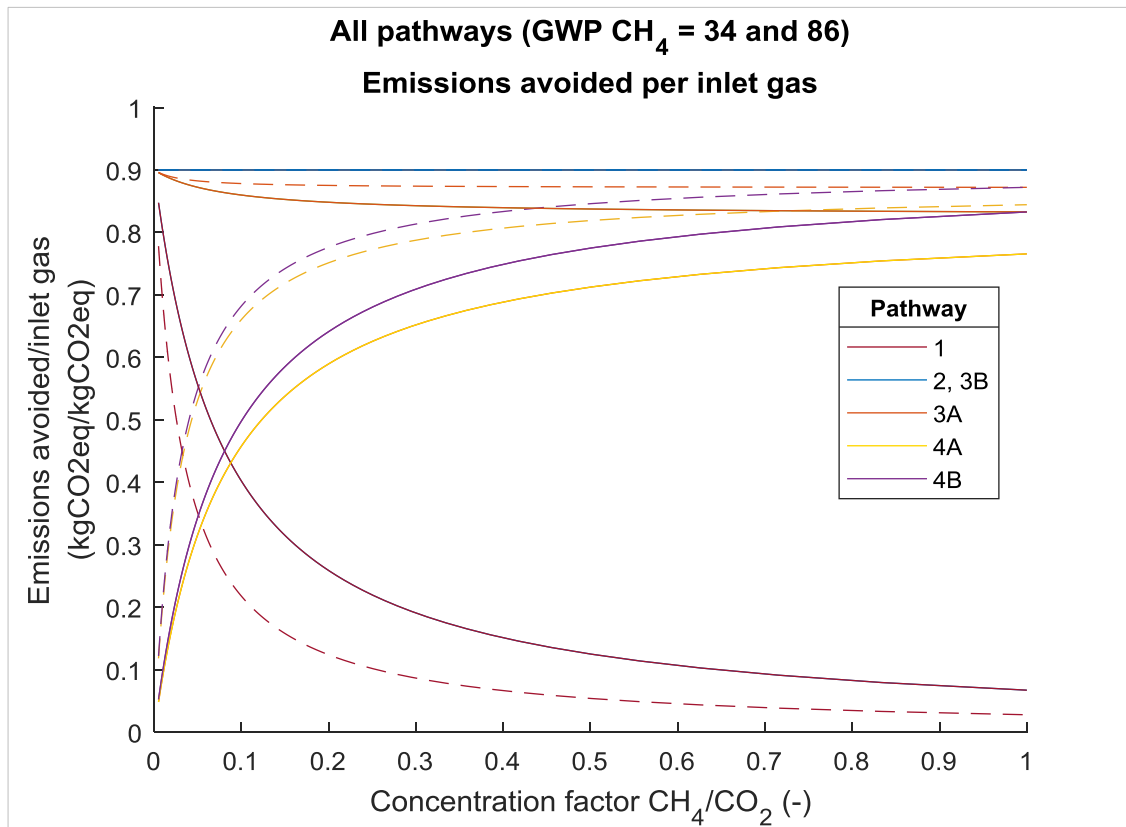


Figure 19. Emissions avoided per inlet gas as a function of CF, for a GWP of CH₄ = 34 (solid lines) and 86 (dashed lines)

The effect of a larger GWP value on emission avoided is shown in figure 19. As expected more emissions are avoided for all pathways with the exception of pathway 1, where the avoided emissions are further reduced. 2 and 3B are restricted by the maximum emissions avoided therefore the effect of a larger GWP cannot be observed until the actual capture efficiencies for the separation processes are optimized. For 4A and 4B a greater increase in avoided emissions is observed when CF on the lower end, but the effect tapers and is not as pronounced as CF approaches 1.

4.4. Case studies: exergy and emissions avoided

Using the results from the qualitative assessment of CH₄ sources, the specific exergy requirements and emissions avoided for an inlet gas composition of air and coal mine ventilation air (VAM) are investigated. Results are displayed in the tables and figures below, accompanied with a discussion of main observations of results. Tables showing the mass and exergy balances (kJ/s) for each component are in Appendix – A. The results shown here will

describe the exergy required and emissions avoided for an inlet gas or the exergy per emissions avoided.

Table 6. Inlet concentrations of CO₂ and CH₄ for emission sources air and VAM (Sources: ESRL, 2018; ibid)

| Concentration in source (ppm) | Component | |
|-------------------------------|-----------------|-----------------|
| | CO ₂ | CH ₄ |
| Air | 400 | 2 |
| VAM | 400 | 15000 |

The concentrations of CO₂ and CH₄ in the emission source are inputted into Matlab, from which the following results were obtained.

4.4.1. Case study 1 – Air

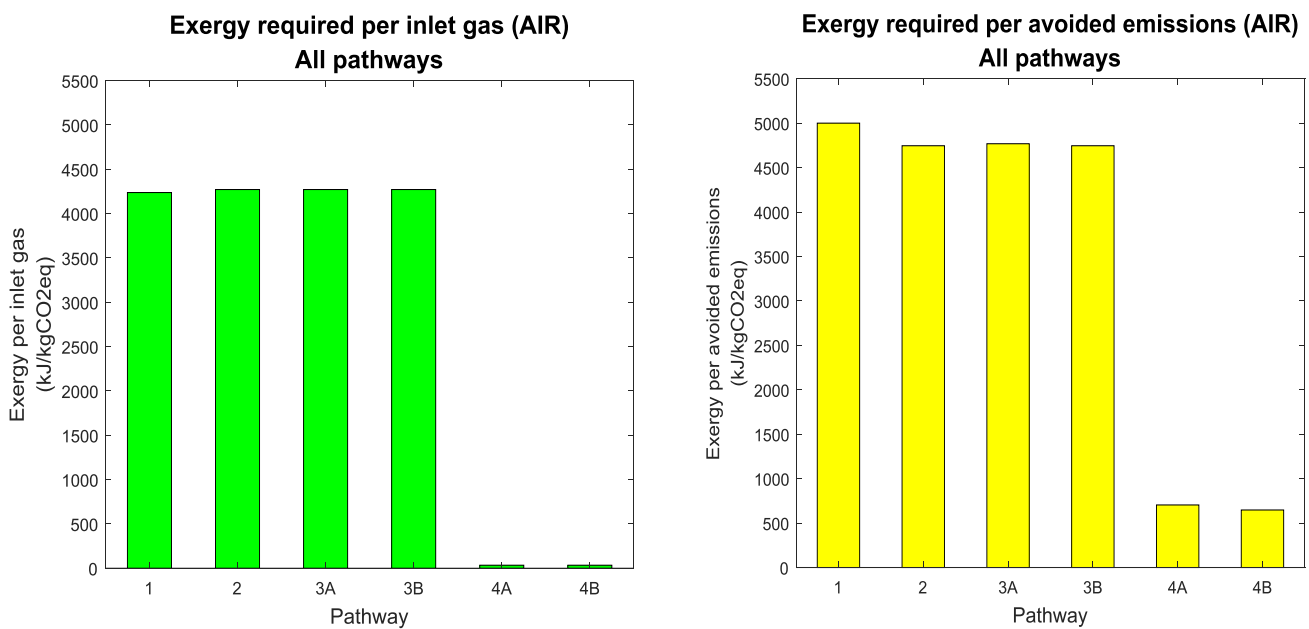


Figure 20. (Case: Air) Amount of exergy required per inlet gas and per avoided emissions (kJ/kgCO₂eq).

The exergy require per inlet gas and per avoided emissions is shown in figure 20. The differences in values are slight therefore values are highlighted in table 7 below to improve interpretation of results.

Table 7. Exergy required for amount of emissions avoided and amount of CO₂ and CH₄ in inlet gas (Case: Air, GWP of CH₄: 34)

| AIR (GWP of CH ₄ : 34) | Exergy required per amount in | | | Exergy required per amount avoided | | |
|-----------------------------------|-------------------------------|----------------------|-------------------------|------------------------------------|----------------------|-------------------------|
| | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq |
| 1 | 4500 | 0 | 4237.41 | 5000 | 0 | 5000 |
| 2 | 4500 | 19805.90 | 4271.41 | 5000 | 22006.56 | 4746.01 |
| 3A | 4500 | 19816.49 | 4271.37 | 5025 | 22018.29 | 4768.41 |
| 3B | 4500 | 19816.74 | 4271.43 | 5000 | 22018.60 | 4746.03 |
| 4A | 0 | 19805.65 | 33.99 | 0 | 22006.24 | 703.87 |
| 4B | 0 | 19805.90 | 33.99 | 0 | 22006.56 | 647.25 |

Main observations

- Given that the low concentration of CH₄ in air compared to CO₂, it is anticipated that the exergy required for separation is high. The exergy required for separation of CO₂ only in pathway 1 is 5000 kJ/kgCO₂. This is expected as the capture efficiency of the technology is assumed to be 90% and as discussed in the method section X., the actual work required for separation of CO₂ from air is 4500 kJ/kgCO₂.
- The work required per kgCO₂eq avoided for 2, 3A and 3B are on the same scale and slightly lower than that of pathway one at 4746, 4768 and 4746 kJ/kgCO₂eq respectively. Even with the much higher work needed for CH₄ separation in these pathways, the contribution of CH₄ to the amount of kgCO₂eq avoided is substantial enough to require less work than CO₂ capture only.
- 3A requires slightly more exergy input per amount avoided which is most likely due to the combustion step whereby more kgCO₂eq is emitted after combustion, compared to 2 and 3B without combustion.
- The lowest work required per avoided emissions are for 4A and 4B at 704 and 647 kJ/kgCO₂eq. Similarly to 3A and 3B, the small difference in values is due to the extra combustion step which results in more CO₂eq emissions.

By comparing the results on this benchmark it can be deduced that capturing either both CH₄ and CO₂, or CH₄ only, requires less exergy per unit of emissions avoided. Furthermore, combustion of CH₄ after capture does not mitigate more CO₂eq than storing the CH₄ after combustion, albeit the difference is minor.

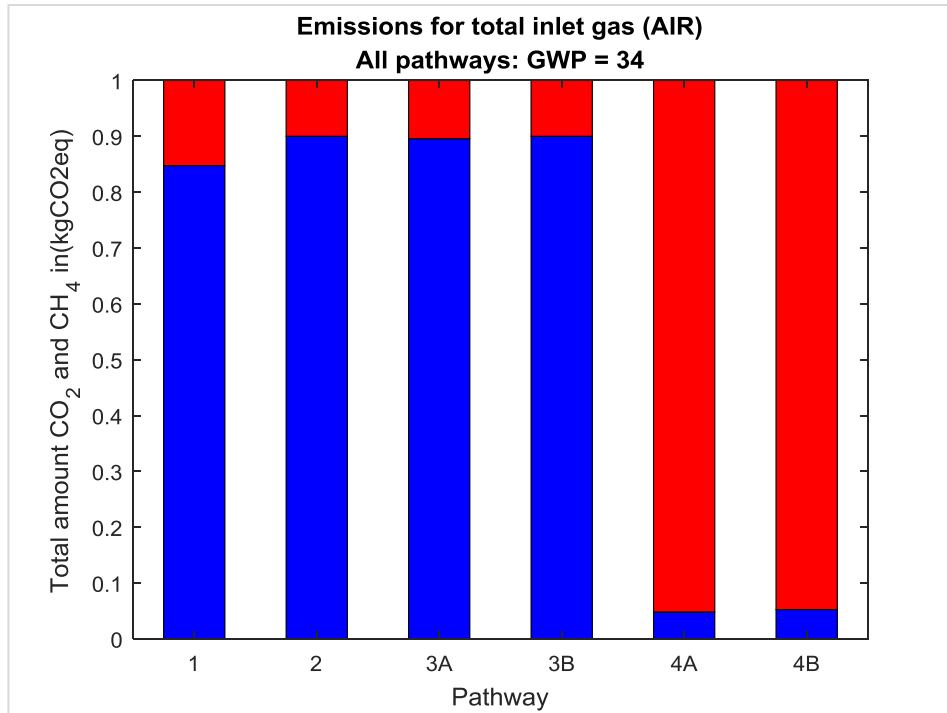


Figure 21. (Case: Air) Avoided emissions per inlet gas (Values shown highlighted below in table 8.

The emissions avoided and emitted per inlet gas are shown in figure 21 and table 8. Given that CH₄ concentrations are low compared to CO₂ in the inlet gas in this case, CO₂eq emissions are only predominantly avoided in pathways which involve both CO₂ and CH₄ capture. Pathway 1 avoids 0.847 kgCO₂eq per inlet gas. 2, 3A and 3B exhibit the largest amount of kgCO₂eq emissions avoided for the inlet gas. However, it is worth mentioning that an initial assumption was inputted stating that the capture efficiency of the technology is at 90%. Therefore, these values would differ depending on the specific efficiency of the capture technology which should be optimized for a specific pathway.

Table 8. (Case: Air) Mass balance for amount of CO₂, CH₄, CO₂ eq, in the inlet gas, emitted and avoided

| AIR | Amount avoided per inlet gas | | | Amount emitted per inlet gas | | |
|-----------|------------------------------|-----------------------|--------------------------|------------------------------|-----------------------|--------------------------|
| Pathway | kgCO ₂ /in | kgCH ₄ /in | kg CO ₂ eq/in | kgCO ₂ /in | kgCH ₄ /in | kg CO ₂ eq/in |
| 1 | 0.9 | 0 | 0.847 | 0.1 | 1 | 0,153 |
| 2 | 0.9 | 0.9 | 0.9 | 0.1 | 0.1 | 0.1 |
| 3A | 0.896 | 0.9 | 0.896 | 0.104 | 0.1 | 0,104 |
| 3B | 0.9 | 0.9 | 0.9 | 0.1 | 0.1 | 0.1 |
| 4A | -4.49 x10 ⁻³ | 0.90 | 0.048 | 1 | 0.1 | 0.952 |
| 4B | -2.85 x10 ⁻¹⁶ | 0.9 | 0.053 | 1 | 0.1 | 0.947 |

As discussed above, the exergy required is low per emissions avoided for 4A and 4B however much less CO₂eq is emitted by the pathways capturing either CO₂ only, or both CO₂ and CH₄. Therefore, for an inlet gas concentration comprised of air, where the CH₄ concentration is low, then it would be more favorable to co-capture CH₄ and CO₂ or moreover by the direct capture of CO₂ only. Pathways 2 and 3B exhibit the highest emissions avoided for a relatively lower amount of work required.

4.4.2. Case study 2 – Coal mine ventilation air (VAM)

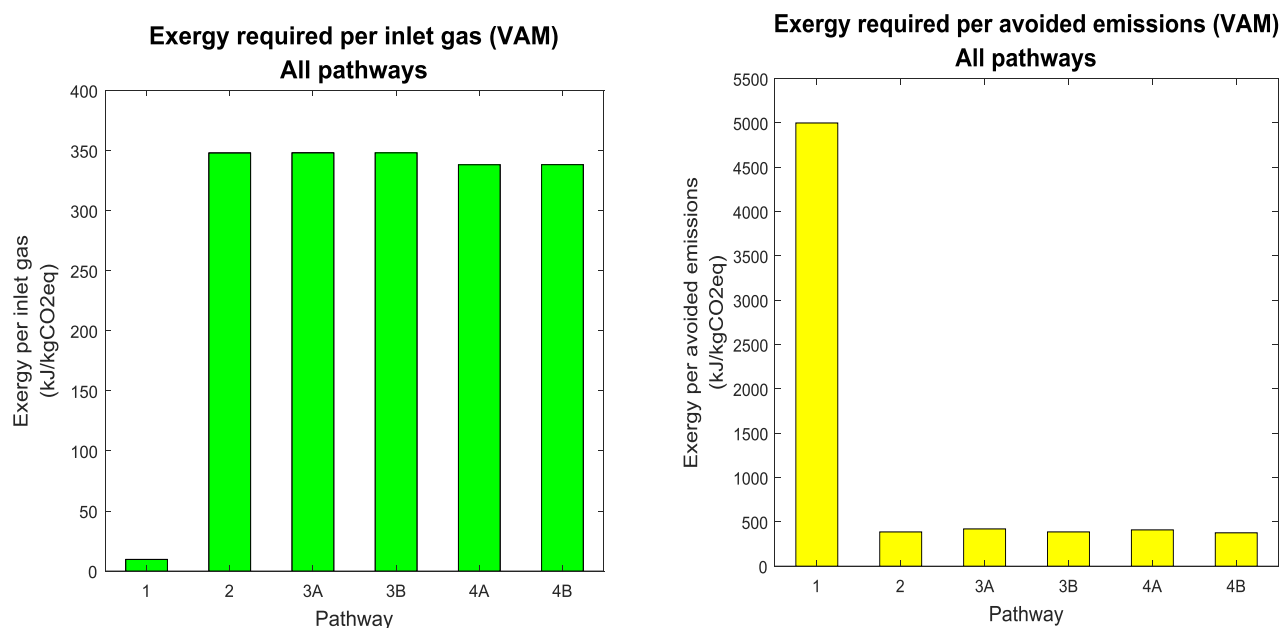


Figure 22. (Case: VAM) Amount of exergy required per avoided emissions (kJ/kgCO₂eq). Value shown in figure are highlighted below

Table 9. Exergy balance for amount of emissions avoided and amount of CO₂ and CH₄ in inlet gas (Case: Coal mine ventilation air (VAM))

| VAM (GWP CH ₄ = 34) | Exergy required per amount in | | | Exergy required per amount avoided | | |
|--------------------------------|-------------------------------|----------------------|-------------------------|------------------------------------|----------------------|-------------------------|
| | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq |
| 1 | 4500 | 0 | 9.66 | 5000 | 0 | 5000 |
| 2 | 4500 | 11528 | 347.99 | 5000 | 12808.7 | 386.65 |
| 3A | 4104 | 11534 | 348.10 | -137 | 12815.6 | 420.62 |
| 3B | 4500 | 11534 | 348.17 | 5000 | 12815.8 | 386.86 |
| 4A | 0 | 11501 | 338.25 | 0 | 12808.5 | 409.68 |
| 4B | 0 | 11528 | 338.33 | 0 | 12808.7 | 376.73 |

Main observations

- In this case the concentration of CH₄ in the inlet gas is higher than that of CO₂, therefore increasing the amount of kgCO₂eq. For pathway 1 the exergy required per inlet gas is very low at 9.66 kJ/kgCO₂eq. This could be explained by the high amount of kgCO₂eq in the inlet gas, coupled with the low exergy required for separation of CO₂

of 27.53 kW (table 2 in appendix). As in the case with air, the exergy required for separation of CO₂ per emissions avoided in pathway 1 is high at 5000 kJ/kgCO₂.

- The exergy required per avoided emission are similar and on the same magnitude for the other pathways involving CH₄ capture, ranging from 377 to 421 kJ/kgCO₂eq avoided. Pathways involving combustion require slightly more work than those that store the product instead.
- In 3A the amount of exergy required for separation of the CO₂ component only is negative at -137 kJ/kgCO₂ because more CO₂ is emitted rather than avoided. This results in the increase in exergy needed compared to the other pathways.
- 2, 3A and 3B result in the lowest exergy per emissions avoided at 387, 387 and 377 kJ/kgCO₂eq.

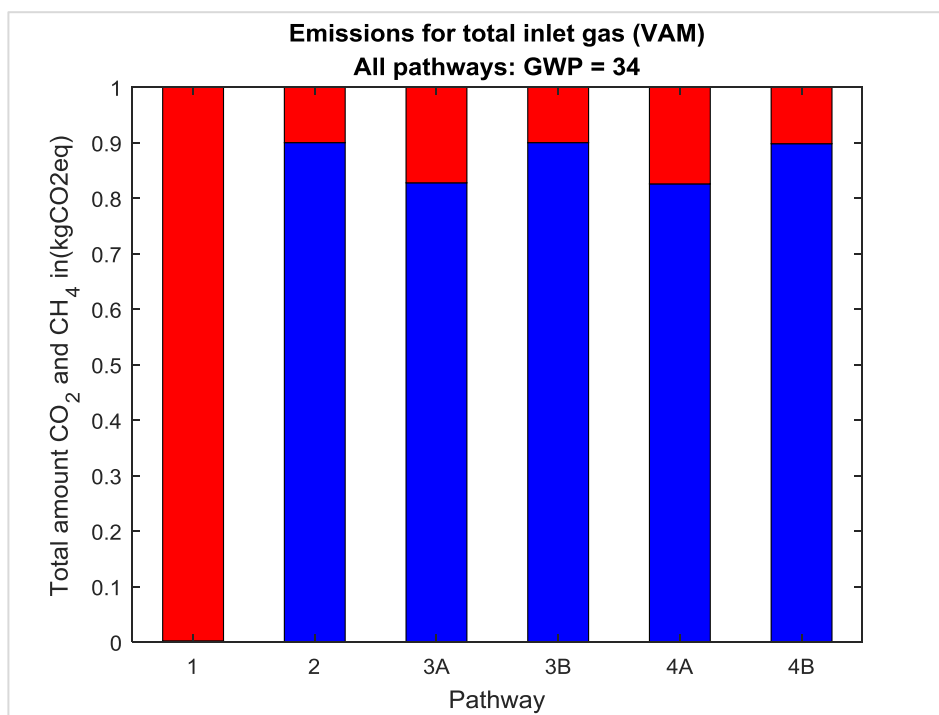


Figure 23. (Case: VAM) Avoided emissions per inlet gas, the unit amount emitted is in red while the amount of emissions avoided are represented by blue. Values shown highlighted below in table 10.

Table 10. (Case: VAM) Amount of emissions avoided per inlet gas for the CO₂, CH₄ components and for overall kgCO₂eq

| VAM | Amount avoided per inlet gas | Amount emitted per inlet gas |
|-----|------------------------------|------------------------------|
| | | |

| Pathway | kgCO ₂ /in | kgCH ₄ /in | kg CO ₂ eq/in | kgCO ₂ /in | kgCH ₄ /in | kg CO ₂ eq/in |
|---------|-----------------------|-----------------------|--------------------------|-----------------------|-----------------------|--------------------------|
| 1 | 0.9 | 0 | 0,0019 | 0.1 | 1 | 0.998 |
| 2 | 0.9 | 0.9 | 0.9 | 0.1 | 0.1 | 0.1 |
| 3A | -29.87 | 0.9 | 0.828 | 30.87 | 0.099 | 0.172 |
| 3B | 0.9 | 0.9 | 0.9 | 0,1 | 0.1 | 0.1 |
| 4A | -30.69 | 0.9 | 0.826 | 31.69 | 0.099 | 0.174 |
| 4B | 0 | 0.9 | 0.898 | 1 | 0.1 | 0.102 |

Due to the higher CH₄ concentration in the VAM gas than CO₂, pathway 1 emits the most kgCO₂eq and no CH₄ is capture and minimal CO₂ is captured. The other pathways show high amount of avoided emissions (table 10: blue), with 2 and 3B having the highest at 0.9 kg CO₂eq avoided. 3A and 4A are shown to emit CO₂ per amount in the inlet gas but the overall kgCO₂eq avoided is still high.

Any of the pathways involving both CO₂ and CH₄ capture or CH₄ capture only exhibit high amount of emissions avoided with low exergy requirements, thus the potential exists for each of those pathways depending on the capture efficiencies of the separation process itself. Taking VAM as the inlet gas, pathway 4B displays the most emissions avoided while having relatively low exergy requirements. The exergy required is 376.73 kJ/kgCO₂eq avoided, and much higher compared to literature where values for CO₂ capture from NGCC flue (~90 kJ/mol CO₂) and for DAC (~400 – 600 kJ/mol CO₂ and higher in some cases) (Wilcox et al., 2017). Nevertheless, the process is yet to be optimized and further studies are needed to determine whether the work needed can be minimized, as the work needed for capture of CH₄ are considerably higher than that for CO₂ capture.

4.4.3. Emissions penalty

When the power source providing the work for the CH₄ capture system has associated emissions, the net CO₂eq removal from the atmosphere is subsequently reduced. It is necessary to ensure the overall system achieves net CO₂eq removal after considering the emission from the source providing the work.

In the most exergetically favorable pathway for CH₄ capture from an inlet gas of VAM (pathway 4B), the exergy requirement is equal to 377 kJ/kgCO₂eq avoided (or 0.1047 MWh/tCO₂eq avoided). Assuming the carbon intensity of the electric grid is 276 kgCO₂/MWh

(European Environment Agency, 2018), then 28.9 kg of CO₂ will be emitted from the power source for every 1 ton of CO₂eq avoided in the pathway . Adding this to the emissions from the pathway of 102 kgCO₂eq/tCO₂eq in, equals 130.9 kgCO₂eq emitted per tCO₂eq avoided.

Likewise for capture from air, in the most favorable pathway 2, the work required is 4746 kJ/kgCO₂eq avoided (or 1.32 MWh/tCO₂eq avoided). Assuming the same carbon intensity from the grid as above, then 364 kg CO₂ is emitted from the power source for every ton of CO₂eq avoided in pathway 2. Adding this to the emissions from the pathway of 100 kgCO₂eq/tCO₂eq in, equals 464 kgCO₂eq emitted per tCO₂eq avoided. This means when avoiding 1 tCO₂eq emission, nearly half of that value is emitted with the power needed to capture the CH₄ and CO₂ from air. Thus, from the perspective of achieving net carbon emissions capturing CH₄ and CO₂ from air through this pathway is constrained unless low carbon energy sources are used directly.

5. Discussion

In this section various aspects of the research will be discussed. Assumptions, limitations, and avenues for further research will be discussed, and also the implications of the results.

CH₄ emissions sources and pathways

During the research it was evident that although CH₄ emission sources are well characterized, it is difficult to quantify the exact volumes and concentrations at which CH₄ was emitted from the source. If uncertainties are reduced in CH₄ measurements, it would be easier to identify potential abatement strategies and current mitigation efforts can be advanced. Moreover the CH₄ emission source selected was chosen based on the criteria and relevance to the particular methodology of this research. The sources may not be the most explored or dominant emissions wise but was suitable for purposes of this study and sub question 1 could be answered.

Furthermore this research was based on a conceptual framework of various CO₂ and/or CH₄ separation pathways. This approach provides a robust comparison of capture/combustion/storage scenarios and a clear overview of the associated work and emissions for a given emissions source. However, processes within the pathways can be further optimized for productivity and storage specifications. Type or costs of a specific storage strategy were not accounted for. For capture and storage of any GHG at some concentration to be economically viable, the storage aspect of must also be inexpensive and technologically feasible. Optimizing the process for minimum work while achieving purity requirements for storage is crucial for capture systems to be implemented.

Thermodynamic versus actual work

For this research various assumptions for made for the methodology and input data. The actual work required for CH₄ separation is based on the performance for capture of CO₂. Since CH₄ capture is only in early development, data for work required are limited. For a real world separation process of CH₄, values may differ from those calculated in this research. Thus the calculations for work required can be interpreted as reasonable but further developments in CH₄ separation processes can perhaps experimentally validate the values obtained in this research.

Results and implications

Results indicate that the capture of gas components with a larger initial concentration in the inlet gas, and from a point source is preferable as opposed to capture from the atmosphere. Taking the GWP of CH₄ into account, the separation pathways demonstrated that although a useful and effective strategy, the mitigation technique of CH₄ combustion is not better at reducing climate effects than storing the CH₄ instead. It was determined that direct capture and storage of CH₄ from a feed inlet gas consisting of ventilation air methane showed the lowest energy requirement at 376 kJ/kgCO₂eq avoided. However this value is substantially larger than current values for CO₂ capture, thus it clear further research will be required to

minimize work required for CH₄ capture, in order for it to take notice as a capable mitigation technology. From these observations sub-question 3 was answered.

The work required is reduced when the target capture component concentration is larger however it is observed from the results that for a given separation pathway, it does not necessarily reflect into more avoided emissions. It is therefore necessary to harmonize the balance between a satisfactory amount of avoided emissions without inducing too much work required. Many elements of the system need to be accounted for, one of many approaches could be procuring the ideal sorbent for the separation process. Assessment of emissions from the power source further establishes this point. It was determined that capture from air using power from the current electricity mix would result in large overall emissions per unit of emissions avoided and thus reduced the purpose of the net negative emission technology. CH₄ capture from VAM exhibited lower overall emissions than that for air capture, separation process or pathway would either have to be optimized in regards to minimizing the work input or else the power source would have to be constrained to low-carbon or CO₂free work.

6. Conclusion

Net emission technologies are acknowledged as a valuable mitigation strategy in the majority emission scenarios to achieve the 1.5°C target. This purpose of this research was to cross-compare potential CO₂ and/or CH₄ capture scenarios with the goal of obtaining the deeper emissions required. The performance of the pathways were successfully assessed based on fundamental thermodynamic principles and the work required and associated emission savings were evaluated. It was determined from the results that the direct capture and storage of CH₄ from coal mine ventilation air shows most promise by achieving a relatively low work requirement while a sufficiently avoiding emissions. Furthermore the power driving the work for the CH₄ capture is most likely constrained to low-CO₂ or CO₂-free work sources to secure the process as a net negative emission technology. By using the GWP of CH₄ and evaluating the thermodynamic requirements for its capture, the research question was thereby answered. This increased understanding of CH₄ capture will support research in developing and improving the capture process on process design level and moreover define implications for possible distributed or point source applications.

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Appendix

A - Case studies

Table 1: (Case: Air) Exergy balance for amount of CO₂, CH₄, CO₂ eq, in the inlet gas

| Air | Exergy required to capture gas component (kW) | | |
|-----|---|-----------------|--------------------|
| | CO ₂ | CH ₄ | CO ₂ eq |
| 1 | 27.349 | 0 | 27.349 |
| 2 | 27.349 | 0.219 | 27.568 |
| 3A | 27.349 | 0.220 | 27.568 |
| 3B | 27.349 | 0.220 | 27.568 |
| 4A | 0 | 0.219 | 0.219 |
| 4B | 0 | 0.219 | 0.219 |

Table 2. The amount of work required to separate CO₂, CH₄, and CO₂eq for the inlet gas concentration of VAM in kW.

| VAM | Exergy required to capture gas component (kW) | | |
|-----|---|-----------------|--------------------|
| | CO ₂ | CH ₄ | CO ₂ eq |
| 1 | 27.53 | 0 | 27.53 |
| 2 | 27.53 | 964.13 | 991.66 |
| 3A | 27.53 | 964.66 | 992.19 |
| 3B | 27.53 | 964.66 | 992.19 |
| 4A | 0 | 964.13 | 964.13 |
| 4B | 0 | 964.13 | 964.13 |

Table 3. (Case: Air) Mass balance for amount of CO₂, CH₄, CO₂ eq, in the inlet gas, emitted and avoided per second

| AIR | Amount in | | | Amount emitted | | | Amount avoided | | |
|-----|----------------------|------------------------|-------------------------|----------------------|---------------------------|-------------------------|------------------------|----------------------|-------------------------|
| | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s |
| 1 | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00061 | 1.10768 x10 ⁻⁵ | 0.00098 | 0.00547 | 0 | 0.0055 |
| 2 | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00061 | 1,11 x10 ⁻⁶ | 0.00065 | 0.00547 | 9.97E-06 | 0.0058 |
| 3A | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00064 | 1,11 x10 ⁻⁶ | 0.00067 | 0.00544 | 9.97E-06 | 0.0058 |
| 3B | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00061 | 1,11E-06 | 0.00065 | 0.00547 | 9.97E-06 | 0.0058 |
| 4A | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00611 | 1,11E-06 | 0.00614 | -2.7x10 ⁻⁵ | 9.969E-06 | 0.0003 |
| 4B | 0.0061 | 1,11 x10 ⁻⁵ | 0.0065 | 0.00608 | 1,11E-06 | 0.00612 | -1.7x10 ⁻¹⁸ | 9,96908 E-06 | 0.0003 |

Table 4. (Case: VAM) Mass balance for amount of CO₂, CH₄, CO₂ eq, in the inlet gas, emitted and avoided per second

| VAM | Amount in | | | Amount emitted | | | Amount avoided | | |
|-----|----------------------|----------------------|-------------------------|----------------------|----------------------|-------------------------|----------------------|----------------------|-------------------------|
| | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s | kgCO ₂ /s | kgCH ₄ /s | kg CO ₂ eq/s |
| 1 | 0.0061 | 0,0836350 | 2.8497 | 0.0006 | 0,0836350 | 2.8442 | 0.00551 | 0 | 0.005507 |
| 2 | 0.0061 | 0,0836350 | 2.8497 | 0.0006 | 0,0083635 | 0.2850 | 0.00551 | 0,0752715 | 2.5647 |
| 3A | 0.0067 | 0,0836361 | 2.8503 | 0.2071 | 0,0083635 | 0.4915 | -0.2004 | 0,0752726 | 2.3589 |
| 3B | 0.0061 | 0,0836350 | 2.8497 | 0.0006 | 0,0083635 | 0.2850 | 0.00551 | 0,0752715 | 2.5647 |
| 4A | 0.0067 | 0,0836361 | 2.8503 | 0.2126 | 0,0083635 | 0.4970 | -0.2059 | 0,0752726 | 2.3534 |
| 4B | 0.0061 | 0,0836350 | 2.8497 | 0.0061 | 0,0083635 | 0.2905 | 0 | 0,0752715 | 2.5592 |

Table 5. Exergy required for amount of emissions avoided and amount of CO₂ and CH₄ in inlet gas (Case: Air, GWP of CH₄: 86)

| AIR (CH ₄ GWP = 86) | Exergy required per amount in | | | Exergy required per amount avoided | | |
|--------------------------------|-------------------------------|----------------------|-------------------------|------------------------------------|----------------------|-------------------------|
| | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq | kJ/kgCO ₂ | kJ/kgCH ₄ | kJ/kgCO ₂ eq |
| 1 | 4500 | 0 | 3890 | 5000 | 0 | 5000 |
| 2 | 4500 | 19806 | 3921.44 | 5000 | 22007 | 4357.16 |
| 3A | 4500 | 19817 | 3921.41 | 5025 | 22019 | 4376.03 |
| 3B | 4500 | 19817 | 3921.46 | 5000 | 22019 | 4357.17 |
| 4A | 0 | 19806 | 31.206 | 0 | 22007 | 264.29 |
| 4B | 0 | 19806 | 31.207 | 0 | 22007 | 255.89 |

