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# Exergy Return on Exergy Investment and CO<sub>2</sub> Intensity of the Underground Biomethanation Process

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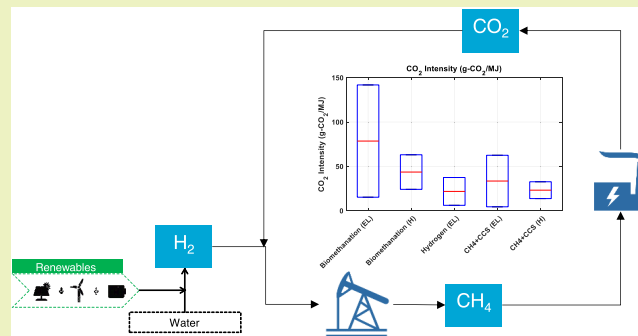
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**ABSTRACT:** This paper presents an assessment of the life-cycle exergetic efficiency and CO<sub>2</sub> footprint of the underground biomethanation process. The subsurface formation, hosting microorganisms required for the reaction, is utilized to convert CO<sub>2</sub> and green (produced from renewable energy) hydrogen to the so-called “green” or synthetic methane. The net exergy gain and CO<sub>2</sub> intensity of the biomethanation process are compared to the alternative options of (1) green H<sub>2</sub> storage (no energy upgrading process to CH<sub>4</sub>) and (2) fossil-based CH<sub>4</sub> with carbon capture and storage (CCS), i.e., blue CH<sub>4</sub>. It is found that with the current state of the technology and within the assumptions of this study, the exergy return on the exergy invested for underground biomethanation does not outperform the direct storage and utilization of green H<sub>2</sub>. The maximum exergetic efficiency of the biomethanation process is calculated to be 15–33% for electricity and 36–47% for heating, while the overall exergetic efficiency of the direct use of H<sub>2</sub> for electricity is estimated to be between 20 and 61%. Moreover, the energy produced from the underground biomethanation process has the largest CO<sub>2</sub> intensity among the studied options. Depending on the technology used in the CCS and hydrogen production stages, the CO<sub>2</sub> intensity of the electricity generated from synthetic CH<sub>4</sub> can be as large as 142 g CO<sub>2</sub>/MJe, which is at least 56–73% larger than those of the two other studied cases.

**KEYWORDS:** hydrogen, energy storage, biomethanation, climate change, synthetic methane, carbon dioxide, subsurface reactor



## INTRODUCTION

Transition toward the supply of the renewable energy, such as wind and solar, depends not only on the development of more efficient and less expensive production technologies but also on the development of large-scale storage systems in the order of TWh. As an example, in the Netherlands with about 17.5 million residents, about 800 TWh energy was consumed in 2020.<sup>1</sup> This number for the USA is roughly 30 000 TWh.<sup>1</sup> One TWh energy is equivalent to 10 million electrical-vehicle batteries of 100 kWh size. Therefore, large-scale energy storage in the form of electricity is not yet feasible. Alternatively, one can store renewable electricity in the form of compressed gas, such as green hydrogen (H<sub>2</sub>) or methane (CH<sub>4</sub>), which is the focus of power-to-gas (P2G) technologies.<sup>2–4</sup> Energy storage in the form of “green” or synthetic CH<sub>4</sub> is seemingly more attractive since it will be produced by the microbial reduction of carbon dioxide (CO<sub>2</sub>) captured from the atmosphere with the green H<sub>2</sub>. It is therefore possible to store renewable energy at the scale of several TWh if subsurface geological reservoirs are utilized to provide huge storage space for the electrochemically manufactured green gases. In that concept, geological reservoirs can not only be used for storage but

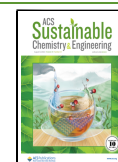
also facilitate upgrading of the energy content of the stored gas (i.e., serve as large (bio)reactors).<sup>5,6</sup> For instance, green H<sub>2</sub> can be stored in subsurface reservoirs to be microbially converted with the already injected or coinjected CO<sub>2</sub> at the in situ thermodynamic conditions and chemical compositions to produce methane.<sup>7–9</sup>

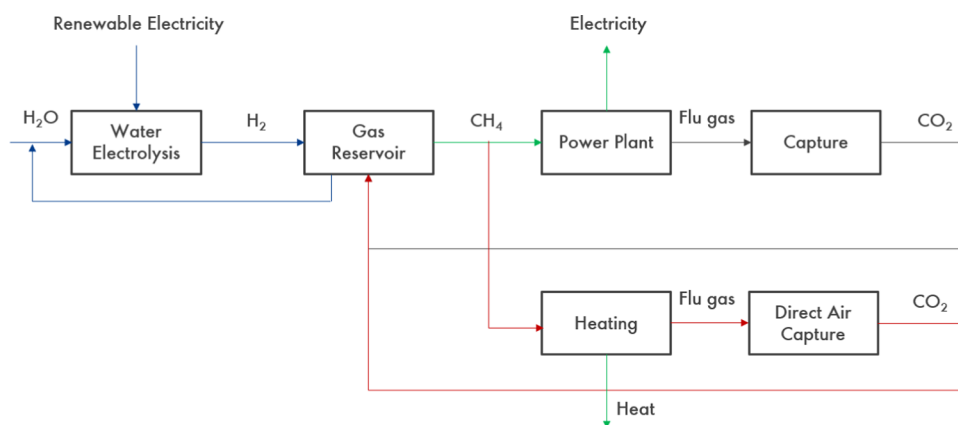
The conversion of CO<sub>2</sub> and H<sub>2</sub> to synthetic methane facilitated by microbes, abundant in subsurface formations, has recently gained a lot of attention.<sup>8,10,11</sup> This concept is referred to as “underground biomethanation”, for which it is suggested to intentionally coinject CO<sub>2</sub> and H<sub>2</sub> into the subsurface formations to (1) produce synthetic CH<sub>4</sub> with larger (volumetric) energy content than H<sub>2</sub> and (2) utilize the captured CO<sub>2</sub>.<sup>8,12</sup> Indeed, the biomethanation process converts 4 moles of H<sub>2</sub> and 1 mole of CO<sub>2</sub> into 1 mole of CH<sub>4</sub> (see eq

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**Figure 1.** Schematic overview of the application of synthetic  $\text{CH}_4$  produced from the underground biomethanation process for heat and electricity supply. The injection of green  $\text{H}_2$  and  $\text{CO}_2$  captured directly from air or from power plants is required to facilitate the reaction.

1). As such, it allows for efficiently utilizing the available storage capacity. The microbial metabolism that plays a central role in the biomethanation conversion process is referred to as methanogenesis and is restricted to a specific strain of microbes called methanogens that belong to the domain of Archaea.<sup>13</sup> Methanogens are commonly sensitive to oxygen and are intrinsically abundant in anaerobic natural and anthropogenic environments (soils, deep subsurface, oil reservoirs, wetlands, digestive tracts, anaerobic wastewater treatment systems, etc.).<sup>13,14</sup> Therefore, methanogens play a critical role in the global carbon cycle through the degradation of the organic material into  $\text{CH}_4$  (a major natural carbon sink). Methanogens have, as is common for other Archaea, the ability to persist and even flourish under extreme conditions (high salinity, high temperature, etc.). In the past decades, carbon capture and storage (CCS) was proposed as a facilitator to generate  $\text{CH}_4$  through methanogenesis in subsurface storage sites.<sup>8</sup> The reducing equivalents required to reduce  $\text{CO}_2$  were proposed to come from the degradation of the organic material (bitumen, oil, gas, etc.) in the storage sites.<sup>15</sup> It is important to emphasize that the subsurface formations often contain  $\text{CO}_2$ , bicarbonate, and/or carbonate. Moreover, the degradation of the organic matter required to produce the reducing equivalents (e.g.,  $\text{H}_2$ ) is a net  $\text{CO}_2$ -generating process. As such, although  $\text{CH}_4$  formation can occur in the subsurface naturally, it is unlikely to be significantly stimulated by the externally injected  $\text{CO}_2$  in the CCS projects. Recent findings, nevertheless, have reported increasing levels of  $\text{CH}_4$  generated from injected  $\text{CO}_2$  and the hydrocarbons fraction through methanogenesis.<sup>47</sup> In the biomethanation process, however, the reducing equivalents to reduce  $\text{CO}_2$  to  $\text{CH}_4$  are provided by the coinjected  $\text{H}_2$ . Biomethanation has been shown to occur in various subsurface storage sites where both  $\text{H}_2$  and  $\text{CO}_2$  are present.<sup>7–9</sup>

For the underground biomethanation to be considered a viable option, it must result in a net-positive  $\text{CO}_2$  storage (i.e., negative emission) as well as be competitive with other energy sources in its carbon intensity, defined as the mass of  $\text{CO}_2$  emitted per unit energy extracted ( $\text{g CO}_2/\text{MJ}$ ). It is, therefore, necessary to examine the full-cycle exergetic efficiency and  $\text{CO}_2$  intensity of this concept and compare it with alternative energy sources. The utilization of blue  $\text{H}_2$  for this process will already be net-carbon negative because the volume of  $\text{CO}_2$  converted to  $\text{CH}_4$  will lag behind the volume of  $\text{CO}_2$  generated during  $\text{H}_2$  production (e.g., in the steam-methane reforming

method) and the  $\text{CO}_2$  capture process itself. Therefore, the analyses performed in this paper only consider the utilization of the green  $\text{H}_2$  generated from low-carbon sources of energy (such as solar or wind).

The two major material streams required for exergy analysis of the biomethanation process are  $\text{H}_2$  and  $\text{CH}_4$ . Hydrogen has the advantage that its oxidation does not produce  $\text{CO}_2$ ; however,  $\text{H}_2$  is a secondary energy source or fuel, i.e., it needs to be produced through an energy-intensive electrolysis process.<sup>16–20</sup> On the other hand, fossil-based  $\text{CH}_4$  or natural gas is an abundant source of energy and the exergy invested in its production is a small portion of its chemical exergy.<sup>21</sup> Nevertheless, the oxidation of  $\text{CH}_4$  produces a significant amount of  $\text{CO}_2$ , which needs to be captured and utilized or stored to reduce its environmental footprint.

The main goal of this study is to examine the full-cycle exergy and  $\text{CO}_2$  intensity of the (underground) biomethanation process and compare it to green  $\text{H}_2$  and fossil-based  $\text{CH}_4$  with the CCS option, referred to as blue  $\text{CH}_4$  in this paper. To provide a reliable quantitative assessment, the concept of exergy return on exergy investment (ERoEI) is chosen for the presented analyses.<sup>22–24</sup> ERoEI is a common method of evaluating the efficiency of energy systems from a thermodynamic point of view. Exergy is the part of energy, which is available to perform useful work. Exergetic efficiency or ERoEI is the fraction of the exergy input (exergy investment) that has been converted to useful work (exergy return). The “lost” or “wasted” exergy is caused by irreversibilities explained by the second law of thermodynamics and is practically responsible for  $\text{CO}_2$  emissions when comparing different fuels. Therefore, the ERoEI concept is useful in ranking different processes and fuels in terms of efficiency and  $\text{CO}_2$  intensity<sup>22</sup> and can be used as a measure of sustainability in comparing various energy systems.

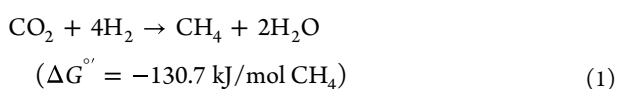
The structure of the paper is as follows. First, the methodology and the underlying assumptions are explained. Afterward, the ERoEI and  $\text{CO}_2$  intensity of the considered options are compared. The paper ends with some concluding remarks.

## METHODOLOGY

Figure 1 shows the schematic of the different stages of the underground biomethanation process. First, green  $\text{H}_2$  is produced by the electrolysis of water using solar energy. The required water can either be supplied from a nearby water

source or the water produced from the gas reservoir. Water should be treated to remove the contaminants or dissolved salts. The produced CH<sub>4</sub> from the reservoir is either sent to a power plant to generate electricity or is used as a heat source in buildings. In both applications, the burning of CH<sub>4</sub> produces CO<sub>2</sub>, which needs to be captured before being emitted into the atmosphere. The captured CO<sub>2</sub> is injected into the reservoir. It is assumed that the capture site is 300 km away from the reservoir. This number can certainly be changed for specific site selection analyses. For each work stream, minimum and maximum values have been taken to account the limitations of the technologies involved, uncertainty range, and process inefficiencies.

**Biomethanation Reaction.** The injection of the mixture of H<sub>2</sub> and CO<sub>2</sub> into the subsurface storage sites in the presence of methanogens under certain conditions can result in production of CH<sub>4</sub> according to



To consider the most efficient biomethanation process, i.e., the best-case scenario, it is assumed that the conversion of eq 1 is 100%. This reaction is exothermic and releases a significant amount of heat. To increase the efficiency of the process, the released heat can be integrated and utilized in the process if the biomethanation process occurs on the surface reactors. Methane is produced through the methanogenesis reaction as described in eq 1 and then goes through the energy-production with the CCS cycle as explained before. For the sake of simplicity, we assume that the reaction is instantaneous and that its conversion is 100%, i.e., 4 moles of H<sub>2</sub> combined with 1 mole of CO<sub>2</sub> produces 1 mole of CH<sub>4</sub>. In other words, to produce 1 kg of CH<sub>4</sub>, 44:16 = 2.75 kg of CO<sub>2</sub> and 8:16 = 0.5 kg of H<sub>2</sub> is required. Given the above-mentioned assumptions, the results of this study are considered to be the best-case scenario; therefore, in practice, the exergetic efficiency of the underground biomethanation process will most likely be smaller than what is reported here.

We compare the CH<sub>4</sub> produced from the underground biomethanation process or synthetic CH<sub>4</sub> with (1) the direct use of H<sub>2</sub> and (2) with the fossil-based CH<sub>4</sub> produced from natural gas reservoirs. The produced H<sub>2</sub> is shipped to the market for use in different applications, for example, in fuel cells to generate electricity. Like the synthetic CH<sub>4</sub>, the fossil-based CH<sub>4</sub> can be used in power plants for electricity generation or as a heat source, albeit to mitigate its negative climate impacts, the generated CO<sub>2</sub> is captured and stored.

**Exergy Analysis.** In this section, we describe the exergy analysis of the system defined in Figure 1 by accounting for material and work streams. The dead state (the state at which the system exergy is zero) is assumed to be at a temperature and a pressure of 298.15 °C and 1 atm (101.325 kPa), respectively. The exergetic efficiency of the system is measured by the magnitude of the exergy return on exergy investment (ERoEI) defined as

$$\text{ERoEI} = \frac{\text{Exergy Return}}{\text{Exergy Invested}} \quad (2)$$

The exergy return is the amount of electricity (MJe) or heat (MJ) produced from the fuel (either H<sub>2</sub> or CH<sub>4</sub>). The invested exergy is the total energy required in different stages of the process accounting for the nonideal nature of the system

dictated by the second law of thermodynamics. Another measure of the sustainability of the fuels is the exergy recovery factor, which is the net exergy gain normalized to the exergy of fuel, i.e.,

$$\text{Ex}_{\text{RF}} = \frac{\text{Ex}_{\text{returned}} - \text{Ex}_{\text{invested}}}{\text{Ex}_{\text{fuel}}} \quad (3)$$

Ex<sub>RF</sub> can vary between  $-\infty$  and 1. A negative Ex<sub>RF</sub> means that the system has invested more exergy than gained; however, this does not necessarily lead to more CO<sub>2</sub> emissions. Ex<sub>RF</sub> > 0 when ERoEI > 1.

**Material Streams.** The main material streams of the system are CH<sub>4</sub>, H<sub>2</sub>, and CO<sub>2</sub>, whose chemical exergy values are assumed to be 52.7 MJ/kg CH<sub>4</sub>, 134 MJ/kg H<sub>2</sub>, and 0.0 MJ/kg CO<sub>2</sub>, respectively.<sup>43</sup> It should be noted that the chemical exergy of gas fuels is estimated from their lower heating value (LHV) and higher heating value (HHV). For H<sub>2</sub>, the chemical exergy is above its LHV (120 MJ/kg H<sub>2</sub>) but slightly below its HHV (142 MJ/kg H<sub>2</sub>).<sup>45</sup>

**Work Streams. Hydrogen Production.** The exergy of H<sub>2</sub> production from water electrolysis is in the range of 180–220 MJe/kg H<sub>2</sub> with a CO<sub>2</sub> intensity of 0.7–2.0 kg CO<sub>2</sub>/kg H<sub>2</sub>.<sup>26,27</sup> We assume that these numbers include water treatment. The exergy required to break the water molecules is supplied from a solar source with a specific CO<sub>2</sub> emission of 12.5 g CO<sub>2</sub>/MJe.<sup>25</sup>

**Hydrogen Compression and Transport.** The exergy required to compress and transport H<sub>2</sub> to the storage site can be as large as 5–20% of its production exergy.<sup>28–30</sup>

**CO<sub>2</sub> Capture and Transport.** The exergy required to capture CO<sub>2</sub> depends on its concentration at the capturing point. For power plants with high concentrations of CO<sub>2</sub>, the commercially available technology utilizes monoethanolamine (MEA) as a solvent to absorb CO<sub>2</sub> from the flue gas stream. The required exergy for capture, transportation, and storage of the MEA-based method could be as high as 3.5–6 MJe/kg CO<sub>2</sub>, with a capturing efficiency of 80–95%.<sup>24,31–34</sup> It is assumed that the capturing energy is provided by the same power plant with an overall process efficiency of 40–63%.<sup>35</sup> When the source of capturing energy is not carbon-free, additional energy will be required to remove the CO<sub>2</sub> resulting from the capturing process itself (energy penalty).<sup>26,31</sup> The energy penalty in the multistage capturing process for gas power plants is estimated to be 25–50% depending on the magnitude of the capturing exergy.<sup>31</sup> When flue gas is directly emitted to air, like in heating or transportation applications, the exergy required to capture CO<sub>2</sub> significantly increases. The value has been reported to be 6.75–9.90 MJe/kg CO<sub>2</sub> with an overall capture efficiency of 50–75%.<sup>26,36,37</sup> To make this a useful practice, the energy required to capture CO<sub>2</sub> directly from the air should be provided from renewable or low-carbon resources.

**Efficiency of Hydrogen Fuel Cells.** Fuel cells convert the chemical exergy of H<sub>2</sub> directly to electricity. For an ideal hydrogen–oxygen fuel cell, the only byproduct is water; however, some of the input exergy is wasted as heat. The conversion efficiency of the fuel cells depends on the reactants, the type of the electrolyte, and the temperature of the reactants.<sup>40</sup> The practical conversion efficiency of hydrogen fuel cells is currently in the range of 40–60%<sup>44</sup> but their efficiency is expected to increase up to 85% if the wasted heat is integrated into the system.<sup>38–40</sup> To have the best estimate

for H<sub>2</sub> fuel, therefore, an overall conversion efficiency of 40–85% was assumed for the hydrogen fuel cells.

**Thermal Efficiency of Gas Heaters.** In accordance with the data published by the US Department of Energy (DOE), in the gas-to-heat route, the thermal efficiency of the gas heaters is considered to be 80% for conventional heaters, which can increase to 90% for highly efficient heaters.<sup>41</sup>

The main assumptions of the calculations are summarized in Table 1 (material streams) and Table 2 (work streams).

**Table 1. Main Material Streams and Their Chemical Exergy**

chemical	chemical formula	M <sub>w</sub> (g/mol)	specific chemical exergy (MJ/kg)
methane	CH <sub>4</sub>	16	52.0
carbon dioxide	CO <sub>2</sub>	44	
hydrogen	H <sub>2</sub>	2	134

**Table 2. Main Assumptions and Input Parameters Used for the Calculations**

work stream		refs
hydrogen production	exergy: 180–220 MJ/kg H <sub>2</sub> specific CO <sub>2</sub> emission: 0.7–2.0 kg CO <sub>2</sub> /kg H <sub>2</sub>	26, 27
hydrogen compression and transport	6–35% of chemical exergy of hydrogen (8.1–46.9 MJ/kg H <sub>2</sub> )	28–30
CO <sub>2</sub> capture and transport	MEA–solvent: 3.5–6 MJ/kg CO <sub>2</sub> with a capture efficiency of 80–95% direct air capture: 6.75–9.9 MJ/kg CO <sub>2</sub> with a capture efficiency of 50–75%	24, 31–34 26, 36, 37
conversion efficiency of the gas power plant	40–63%	35
conversion efficiency of the hydrogen fuel cell	40–85%	39, 40, 44
thermal efficiency of the gas heater	80–90%	41

## RESULTS AND DISCUSSION

**Electricity–Hydrogen–Electricity.** Based on the numbers provided in Tables 1 and 2, the power required to manufacture, compress, and transport H<sub>2</sub> will be in the range of 188.1–266.9 MJ/kg H<sub>2</sub>. On the other hand, to convert the chemical exergy of H<sub>2</sub> to electricity, the conversion efficiency of fuel cells should be considered, which means that 1 kg of H<sub>2</sub> will generate 53.6–113.9 MJ of electricity (MJe). Therefore, for this system, the minimum and maximum ERoEI are  $ex_{inv,min}^{H_2,E} = 53.6/266.9 = 0.20$  and  $ex_{inv,max}^{H_2,E} = 113.9/188.1 = 0.61$ , respectively. This indicates that during the conversion of electricity to H<sub>2</sub> and H<sub>2</sub> to electricity, about 39–80% of the invested exergy is lost or wasted. The minimum CO<sub>2</sub> intensity of the electricity generated from this route is calculated as

$$e_{CO_2,min}^{H_2,E} = 0.70 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{H}_2} \times \frac{1}{188.1} \frac{\text{kg} - \text{H}_2}{\text{MJe}} \times \frac{1}{0.61} \times 1000 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CO}_2} = 6.10 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \quad (4)$$

Similarly, the maximum CO<sub>2</sub> intensity of this route is

$$e_{CO_2,max}^{H_2,E} = 2.0 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{H}_2} \times \frac{1}{266.9} \frac{\text{kg} - \text{H}_2}{\text{MJe}} \times \frac{1}{0.20} \times 1000 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CO}_2} = 37.46 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \quad (5)$$

The minimum and maximum exergy recovery factors are calculated using eq 3, i.e.,

$$Ex_{RF,max}^{H_2,E} = \frac{113.9 - 188.1}{134} = -0.55 \quad (6)$$

$$Ex_{RF,min}^{H_2,E} = \frac{53.6 - 266.9}{134} = -1.59 \quad (7)$$

The negative exergy factors indicate that the MJe obtained from the power–H<sub>2</sub>–power route is less than MJe invested during the processes involved. The major contributors to the negative Ex<sub>RF</sub> or smaller than one ERoEI are the large exergy consumption in the water electrolysis stage and the low conversion efficiency of the fuel cells.

**Fossil-Based Methane with CCS–Electricity.** Natural gas is a primary fuel, meaning that it has been produced over geological times in the subsurface formations without providing external exergy. However, exergy is required for its production to the surface, compression, and transportation, which amounts to electricity consumption equivalent to 5–15% of its chemical exergy (2.6–7.8 MJ/kg CH<sub>4</sub>), depending on the complexity of the gas reservoir.<sup>21,46</sup> Moreover, significant exergy should be spent to abate the CO<sub>2</sub> arising from power generation by natural gas. From the oxidation reaction of CH<sub>4</sub>, burning CH<sub>4</sub> in a power plant produces at least 2.75 kg CO<sub>2</sub>/kg CH<sub>4</sub>, which needs to be captured with an exergy requirement of 10.55–20.58 MJ/kg CH<sub>4</sub>, i.e.,

$$ex_{capture,min} = 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \left( 3.5 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} + 0.05 \times 6.75 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \right) = 10.55 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \quad (8)$$

$$ex_{capture,max} = 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \left( 6 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} + 0.15 \times 9.9 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \right) = 20.58 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \quad (9)$$

where 3.5 and 6.0 MJ/kg CO<sub>2</sub> are taken from Table 2. To calculate the minimum exergy, it has been assumed that the required power is supplied from a low-carbon source. Also, it has been assumed that emitted CO<sub>2</sub> from the production of natural gas is dispersed and therefore exergy related to the DAC method was used in the calculations. This means that  $13.15 < ex_{inv}^{bCH_4,E} < 28.38 \frac{\text{MJe}}{\text{kg} - \text{CH}_4}$ .

With a conversion efficiency of 40–63% for gas power plants,<sup>35</sup> burning CH<sub>4</sub> with a specific chemical exergy of 52.0 MJ/kg CH<sub>4</sub><sup>31</sup> generates 20.8–32.8 MJ/kg CH<sub>4</sub> in the form of

electricity. Therefore, gas-fueled power plants will generate electricity with a CO<sub>2</sub> intensity of 83.8–132.2 g CO<sub>2</sub>/MJe if their produced CO<sub>2</sub> is not captured. The exergy spent on the production of the gas and CO<sub>2</sub> capture generates additional CO<sub>2</sub>

$$\begin{aligned} \text{minimum: } & 13.15 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \times 12.5 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \\ & = 164.37 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (10)$$

$$\begin{aligned} \text{maximum: } & 28.38 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \times 132.2 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \\ & = 3751.84 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (11)$$

In case the electricity generated in the same gas power plant is utilized for capturing CO<sub>2</sub>, then the minimum CO<sub>2</sub> intensity of the CCS process is around 1102 g CO<sub>2</sub>/kg CH<sub>4</sub>. Finally, with a capture efficiency of 80–95% the specific emitted CO<sub>2</sub> per MJe of this system is

$$\begin{aligned} e_{\text{CO}_2, \text{min}}^{\text{bCH}_4, \text{E}} &= (2750 + 164.37) \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \frac{1}{32.8} \frac{\text{kg} - \text{CH}_4}{\text{MJe}} \\ &\quad \times (1 - 0.95) \\ &= 4.44 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \end{aligned} \quad (12)$$

$$\begin{aligned} e_{\text{CO}_2, \text{max}}^{\text{bCH}_4, \text{E}} &= (2750 + 3751.84) \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \frac{1}{20.8} \\ &\quad \frac{\text{kg} - \text{CH}_4}{\text{MJe}} \times (1 - 0.80) \\ &= 62.52 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \end{aligned} \quad (13)$$

In case power is supplied from the gas power plant, the minimum intensity of the electricity is 5.87 g CO<sub>2</sub>/MJe. The minimum and maximum ERoEI of this system is calculated to be 0.76 and 2.58, respectively. The greater than 1 ERoEI is due to no exergy investment in the manufacturing of CH<sub>4</sub>.

Finally, the minimum and maximum exergy factors are calculated as

$$\text{Ex}_{\text{RF}, \text{max}}^{\text{bCH}_4, \text{E}} = \frac{32.8 - 12.7}{52.0} = 0.37 \quad (14)$$

$$\text{Ex}_{\text{RF}, \text{min}}^{\text{bCH}_4, \text{E}} = \frac{20.8 - 27.4}{52.0} = -0.13 \quad (15)$$

Without the CCS, 0.25 < Ex<sub>RF</sub> < 0.58, which indicates that 23–38% of the chemical exergy of the natural gas should be spent to abate its CO<sub>2</sub>.

**Fossil-Based Methane with CCS–Heat.** In this route, CH<sub>4</sub> is distributed through the gas networks for heating the residential and commercial buildings. Assuming a medium-to-high heating efficiency of 85–95% in the boiler and heaters,<sup>41</sup> burning methane provides 44.2–49.4 MJ/kg CH<sub>4</sub> in the form of thermal energy with a CO<sub>2</sub> intensity of 135.9–121.6 g CO<sub>2</sub>/MJ heat. The resulting CO<sub>2</sub> is emitted directly into the air in a dispersed manner and consequently exergetically expensive DAC technologies are required to mitigate against this option (see Table 2).

The exergy of CCS for this route can be calculated as

$$\begin{aligned} \text{ex}_{\text{capture}, \text{min}} &= 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 6.75 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \\ &= 18.1 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (16)$$

$$\begin{aligned} \text{ex}_{\text{capture}, \text{max}} &= 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 9.9 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \\ &= 27.2 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (17)$$

Adding the exergy of gas production, 20.7 < ex<sub>inv</sub><sup>bCH<sub>4</sub>,H</sup> < 35.0  $\frac{\text{MJe}}{\text{kg} - \text{CH}_4}$ , which, in turn, results in the production of additional CO<sub>2</sub> with a minimal/maximal amount of

$$\begin{aligned} \text{minimum: } & 20.7 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \times 12.5 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \\ &= 258.34 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (18)$$

$$\begin{aligned} \text{maximum: } & 35 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \times 12.5 \frac{\text{g} - \text{CO}_2}{\text{MJe}} \\ &= 437.81 \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (19)$$

With a CO<sub>2</sub> capture efficiency of 50–75% for the DAC technologies, the CO<sub>2</sub> intensity of the heat generated by this route is

$$\begin{aligned} e_{\text{CO}_2, \text{min}}^{\text{bCH}_4, \text{H}} &= (2750 + 258.34) \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \frac{1}{49.4} \frac{\text{kg} - \text{CH}_4}{\text{MJ}} \\ &\quad \times (1 - 0.75) \\ &= 13.7 \frac{\text{g} - \text{CO}_2}{\text{MJ}} \end{aligned} \quad (20)$$

$$\begin{aligned} e_{\text{CO}_2, \text{max}}^{\text{bCH}_4, \text{H}} &= (2750 + 437.81) \frac{\text{g} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times \frac{1}{44.2} \frac{\text{kg} - \text{CH}_4}{\text{MJ}} \\ &\quad \times (1 - 0.50) \\ &= 32.67 \frac{\text{g} - \text{CO}_2}{\text{MJ}} \end{aligned} \quad (21)$$

The minimum and maximum ERoEI of this system are calculated to be 1.26 and 2.39, respectively. These numbers correspond to

$$\text{Ex}_{\text{RF}, \text{max}}^{\text{bCH}_4, \text{H}} = \frac{49.4 - 20.7}{52.0} = 0.55 \quad (22)$$

$$\text{Ex}_{\text{RF}, \text{min}}^{\text{bCH}_4, \text{H}} = \frac{44.2 - 35.0}{52.0} = 0.18 \quad (23)$$

**Electricity–Hydrogen–Methane–Electricity (Synthetic Methane to Electricity).** Based on the calculations of the previous section, the total captured CO<sub>2</sub> from the CH<sub>4</sub>-to-electricity route is

$$\begin{aligned} \text{minimum: } & (2.75 + 0.164) \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 0.95 \\ & = 2.77 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (24)$$

$$\begin{aligned} \text{maximum: } & (2.750 + 3.75) \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 0.80 \\ & = 5.20 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \end{aligned} \quad (25)$$

These amounts are greater than the CO<sub>2</sub> required in the biomethanation reaction (2.75 kg CO<sub>2</sub>/kg CH<sub>4</sub>). This also indicates that burning the synthetic CH<sub>4</sub> (or fossil-based CH<sub>4</sub>) will emit 0.15–1.95 kg CO<sub>2</sub>/kg CH<sub>4</sub> when combined with CCS. To produce 1 kg of CH<sub>4</sub> from the biomethanation reaction, 0.5 kg of H<sub>2</sub> is needed, which, in turn, adds 0.35–1.0 kg CO<sub>2</sub>/kg CH<sub>4</sub> emission to the chain. This is only the CO<sub>2</sub> emitted from the electrolysis process. Transportation of H<sub>2</sub> to the injection well and its compression also require energy, which are ignored here. Therefore, in an ideal scenario, the production of methane from the biomethanation reaction leads to net CO<sub>2</sub> emission of 0.50–2.95 kg CO<sub>2</sub>/kg CH<sub>4</sub> or 15.24–141.83 g CO<sub>2</sub>/MJe.

The exergy investment is the sum of the exergies of the H<sub>2</sub> production and the CCS process, i.e.,

$$\begin{aligned} \text{ex}_{\text{inv,min}}^{\text{sCH}_4,\text{E}} &= 0.5 \frac{\text{kg} - \text{H}_2}{\text{kg} - \text{CH}_4} \times 180 \frac{\text{MJe}}{\text{kg} - \text{H}_2} \\ &+ 2.77 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 3.5 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \times 0.95 \\ &= 99.2 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (26)$$

$$\begin{aligned} \text{ex}_{\text{inv,max}}^{\text{sCH}_4,\text{E}} &= 0.5 \frac{\text{kg} - \text{H}_2}{\text{kg} - \text{CH}_4} \times 220 \frac{\text{MJe}}{\text{kg} - \text{H}_2} \\ &+ 5.20 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 6 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \times 0.80 \\ &= 135.0 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (27)$$

It is notable that the largest fraction of the exergy investment is in the production of the green H<sub>2</sub>. Based on these numbers, the ERoEI of the underground biomethanation process is calculated to be between 20.8/135 = 0.15 and 32.8/99.2 = 0.33. The maximum and minimum exergy recovery factors are

$$\text{Ex}_{\text{RF,max}}^{\text{sCH}_4,\text{E}} = \frac{32.8 - 99.2}{0.5 \times 134} = -0.99 \quad (28)$$

$$\text{Ex}_{\text{RF,min}}^{\text{sCH}_4,\text{E}} = \frac{20.8 - 135}{0.5 \times 134} = -1.70 \quad (29)$$

**Electricity–Hydrogen–Methane–Heat (Synthetic Methane to Heat).** Following the calculations in the previous sections, the conversion of chemical exergy of synthetic CH<sub>4</sub> to heat (combined with CCS) results in a net CO<sub>2</sub> emission of 1.1–2.59 kg CO<sub>2</sub>/kg CH<sub>4</sub> including the CO<sub>2</sub> emission from H<sub>2</sub> production. These amounts are smaller than the CO<sub>2</sub> required in the biomethanation reaction. Therefore, to complete the reaction, additional CO<sub>2</sub> (0.16–1.65 kg CO<sub>2</sub>/kg CH<sub>4</sub>) should be supplied to the “underground bioreactor”. This requires

exergy investment in the range of 0.16 × 6.75 = 1.08 to 1.65 × 9.9 = 16.33 MJe/kg CH<sub>4</sub> with an additional CO<sub>2</sub> emission of 13.5–204.2 g CO<sub>2</sub>/kg CH<sub>4</sub> (using solar electricity). Therefore, the total net CO<sub>2</sub> emission from this route is 1.23–2.79 kg CO<sub>2</sub>/kg CH<sub>4</sub>, which means that the heat obtained from synthetic CH<sub>4</sub> will eventually have a CO<sub>2</sub> intensity of 24.9–63.1 g CO<sub>2</sub>/MJ heat.

The exergy investment of this route is calculated as

$$\begin{aligned} \text{ex}_{\text{inv,min}}^{\text{sCH}_4,\text{H}} &= 0.5 \frac{\text{kg} - \text{H}_2}{\text{kg} - \text{CH}_4} \times 180 \frac{\text{MJe}}{\text{kg} - \text{H}_2} \\ &+ 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 6.75 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \times 0.75 \\ &= 103.9 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (30)$$

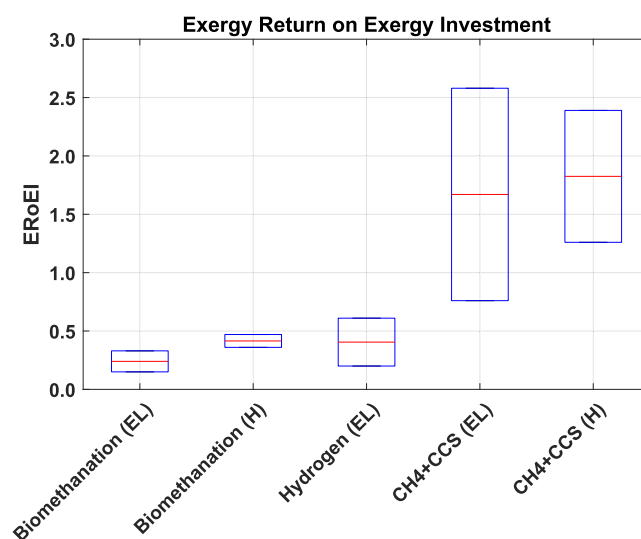
$$\begin{aligned} \text{ex}_{\text{inv,max}}^{\text{sCH}_4,\text{H}} &= 0.5 \frac{\text{kg} - \text{H}_2}{\text{kg} - \text{CH}_4} \times 220 \frac{\text{MJe}}{\text{kg} - \text{H}_2} \\ &+ 2.75 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{CH}_4} \times 9.9 \frac{\text{MJe}}{\text{kg} - \text{CO}_2} \times 0.50 \\ &= 123.6 \frac{\text{MJe}}{\text{kg} - \text{CH}_4} \end{aligned} \quad (31)$$

Consequently, the minimum and maximum ERoEI of this route are estimated to be 0.36–0.47 MJe/MJ heat, respectively. The maximum and minimum exergy recovery factors are

$$\text{Ex}_{\text{RF,max}}^{\text{sCH}_4,\text{H}} = \frac{49.4 - 103.9}{0.5 \times 134} = -0.81 \quad (32)$$

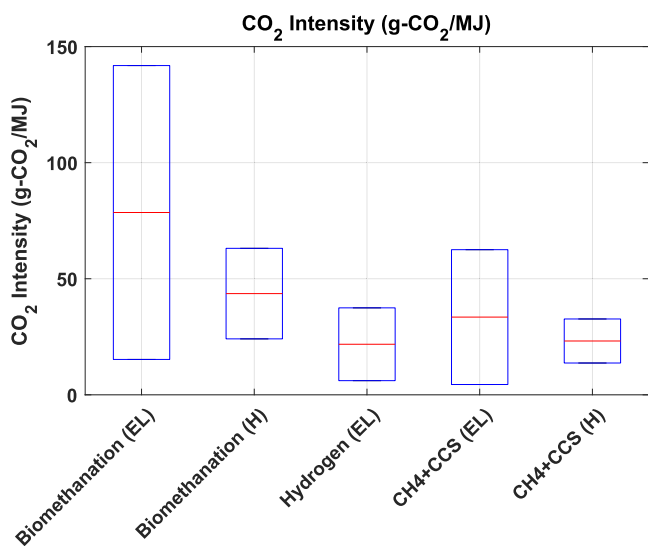
$$\text{Ex}_{\text{RF,min}}^{\text{sCH}_4,\text{H}} = \frac{44.2 - 123.6}{0.5 \times 134} = -1.18 \quad (33)$$

**Comparison with the Direct Use of Methane and Hydrogen.** Figure 2 summarizes the exergy efficiency or exergy return on exergy investment (ERoEI) of the green or synthetic CH<sub>4</sub> produced from the underground biomethana-

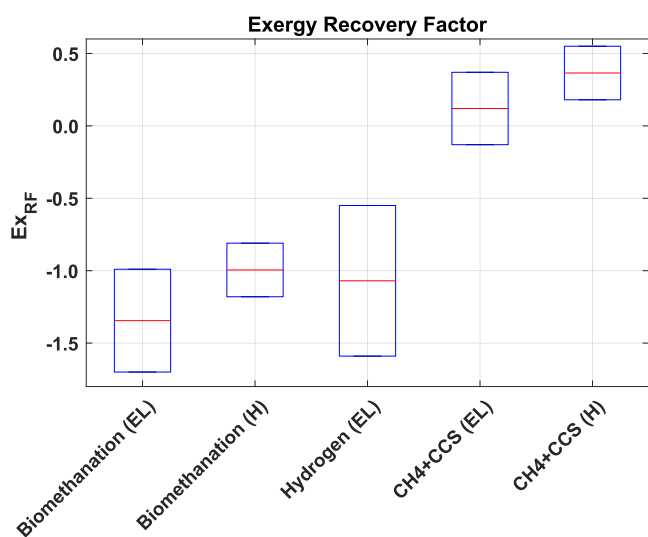


**Figure 2.** Exergy return on the exergy investment (ERoEI) for the biomethanation process (green or synthetic methane) compared to the direct use of hydrogen and CH<sub>4</sub> with CCS (blue methane). H stands for heat or thermal energy and EL stands for electricity.

tion process and compares it with the direct use of H<sub>2</sub> and “blue” CH<sub>4</sub> or CH<sub>4</sub> with the CCS option. The corresponding CO<sub>2</sub> intensity of the different cases and their exergy recovery factors are shown in Figures 3 and 4. Naturally, blue CH<sub>4</sub> has



**Figure 3.** CO<sub>2</sub> intensity of the energy obtained from the biomethanation process (green or synthetic methane) compared to the direct use of hydrogen and CH<sub>4</sub> with CCS (blue methane). H stands for heat or thermal energy and EL stands for electricity.



**Figure 4.** Exergy recovery factor, defined in eq 3, for the biomethanation process (green or synthetic methane) compared to the direct use of hydrogen and CH<sub>4</sub> with CCS (blue methane). H stands for heat or thermal energy and EL stands for electricity.

the largest ERoEI, which is due to the combined effects of its low production exergy and high chemical exergy. Compared to the synthetic CH<sub>4</sub>, the direct use of H<sub>2</sub> for electricity has a larger ERoEI.

The overall exergetic efficiency of the biomethanation process is calculated to be 15–33% for the electricity route and 36–47% for the heating route, while the overall exergetic efficiency of H<sub>2</sub> is 20–61%. The smaller than 1 ERoEI results in a negative exergy recovery factor for these scenarios, indicating that the invested exergy exceeds the gained exergy. Furthermore, apart from having the lowest ERoEI, the energy

produced from the biomethanation process (in the form of electricity or heat) has the largest CO<sub>2</sub> intensity. Depending on the technology used in the CCS and H<sub>2</sub> production stages, the CO<sub>2</sub> intensity of the electricity generated from the synthetic CH<sub>4</sub> can be as large as 142 g CO<sub>2</sub>/MJe, which is at least 56–73% more than the two other cases. The heat generated from the synthetic CH<sub>4</sub> has also more than 50% CO<sub>2</sub> intensity compared to the fossil-based CH<sub>4</sub> with the CCS option. The results are summarized in Table 3.

Based on the ideal assumptions of this study, when overall exergetic efficiency (expressed as ERoEI) and CO<sub>2</sub> footprint are considered, biomethanation appears to be a relatively complex and less efficient process. Moreover, although biomethanation has the benefit of having a huge “reactor” size and residence time, this benefit is largely outweighed by the negative aspects. These negative aspects include limited mixing and diffusion in porous reservoirs causing segregation of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. Other complications are due to limited controllability on the in situ reactive conditions (as compared to bioreactors at surface-based reactors), and most importantly, high possibility of H<sub>2</sub> loss in the reservoir especially due to the generation of contaminants through other microbial processes e.g., acetogenesis and sulfate reduction resulting in the contamination of the aimed CH<sub>4</sub> with, e.g., H<sub>2</sub>S.

The lack of an existing infrastructure for H<sub>2</sub> production and distribution is, however, a major drawback for (commercial and decentralized) the application of H<sub>2</sub>. The current natural gas infrastructure can be used to safely transport up to 10% H<sub>2</sub> in the mixture.<sup>42</sup> Therefore, the production of CH<sub>4</sub> from excess H<sub>2</sub> and CO<sub>2</sub> captured from anthropogenic sources through either surface- or subsurface-based biomethanation can potentially feed the already-existing gas network. Due to the above-mentioned risks associated with the underground biomethanation, surface conversion of H<sub>2</sub> to CH<sub>4</sub> is considered more preferable, although the results presented in Figures 2–4 will still hold.

## CONCLUSIONS

The utilization of subsurface geological reservoirs for energy transition and climate actions is crucially important, as for their scale and scope of contribution to both topics. These giant reservoirs not only provide massive space for green gas storage but also can act as natural reactors. In this work, we assess the life-cycle exergy gain and net CO<sub>2</sub> emission factor of the underground biomethanation process. H<sub>2</sub> and CO<sub>2</sub> are assumed to be coinjected in the reservoir, which also hosts methanogenic Archaea necessary to enhance the in situ microbial reaction. Assuming a reaction conversion of 100%, the maximum exergy gain and CO<sub>2</sub> footprint of the biomethanation process are obtained and compared with the alternative options of green H<sub>2</sub> (no energy upgrading process to CH<sub>4</sub>) and fossil-based CH<sub>4</sub> with CCS (blue CH<sub>4</sub>).

It is found that with the current state of the technology, and considering the ideal assumptions of this study, the exergy return on the exergy invested for the underground biomethanation process does not outperform the direct utilization of the green H<sub>2</sub>. However, more infrastructure should be developed for H<sub>2</sub> to be used on a commercial scale.

The main advantage of the biomethanation process is the possibility to use the already-existing natural gas infrastructure. However, if chosen as a storage molecule, it is favorable to produce the synthetic CH<sub>4</sub> by microbial and/or thermochem-



**Table 3. Upper and Lower Bounds of Exergetic Efficiency and CO<sub>2</sub> Intensity of the Biomethanation Process Compared with Hydrogen and CH<sub>4</sub> + CCS**

	biomethanation (heat)	biomethanation (electricity)	hydrogen (electricity)	CH <sub>4</sub> + CCS (electricity)	CH <sub>4</sub> + CCS (heat)
ERoEI <sub>max</sub> (%)	0.47	0.33	0.61	2.58	2.39
ERoEI <sub>min</sub> (%)	0.36	0.15	0.20	0.76	1.26
minimum CO <sub>2</sub> intensity (g CO <sub>2</sub> /MJe or MJ heat)	24.10	15.24	6.10	4.44	13.7
maximum CO <sub>2</sub> intensity (g CO <sub>2</sub> /MJe or MJ heat)	63.10	141.83	37.46	62.52	32.67
Ex <sub>RF,max</sub>	−0.81	−0.99	−0.55	0.37	0.55
Ex <sub>RF,min</sub>	−1.18	−1.70	−1.59	−0.13	0.18

ical processes at the surface, and subsequently store it in the subsurface either in salt caverns or depleted gas reservoirs.

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### Notes

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