

Comparative Technoeconomic Analysis of Renewable Generation of Methane Using Sunlight, Water, and Carbon Dioxide



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Thirty-one percent of the primary energy consumed in the United States comes from the burning of natural gas, 70–90% of which is composed of methane (CH_4).¹ Natural gas is recovered from onshore and offshore natural gas and oil wells and from coal beds. Currently, the United States has enough supply of dry natural gas to sustain current consumption for 92 years.² Meanwhile, California consumes 2.14 MMcf (43.2 million tons) of natural gas per year,² over a quarter of which is used to generate electric power³ and which provides approximately 40% of the electrical energy in the state.⁴ Because an extensive nationwide storage and distribution network already exists for natural gas, the development of renewable CH_4 could enable rapid and widespread distribution of zero-carbon energy services. Thus, for California to meet its renewable portfolio standard, that is, 60% renewable energy for electricity generation by 2030,⁵ and to conserve a limited resource, it is imperative to assess how to develop and deploy technologies for renewable generation of CH_4 in the next decade.

While an increasing number of power-to-gas (PtG) projects for CH_4 generation or H_2 generation are being planned globally,⁶ the largest source of renewable CH_4 currently being produced in the United States comes from anaerobic digesters that convert cow manure into natural gas. There are currently over 250 such systems in operation with more under construction.⁷ In addition to generating CH_4 renewably, these anaerobic digesters also prevent the release of CH_4 —one of the most potent greenhouse gases—into the atmosphere. However, colocation of dairy farms and anaerobic digesters alone will not yield enough renewable methane to replace the current energy demand met by natural gas.⁸ For example, the residential natural gas demand in California is ~25,000 ton/day,⁴ while an average dairy farm can produce only ~5 ton/day of natural gas from anaerobic digesters.^{7,9} If all potential biogas in California was realized it could power 180,000 homes or 435,000 vehicles, which represents approximately 1.2% of all homes or 3% of all registered vehicles in the state.⁸ While these anaerobic digesters colocated with dairy farms may seem to have small production capacity, they are among the largest sources of renewable CH_4 generation in the world.⁶ Therefore, it is important to evaluate other more readily scalable technology pathways for renewable generation of CH_4 .

Here we outline multiple technology routes for renewable generation of CH_4 from sunlight, water (H_2O), and carbon dioxide (CO_2) (Figures 1 and 2). We evaluate the technology readiness level (TRL), the demonstrated scale of these candidate technologies, the cost for CH_4 generation, as well as the cost required to provide the necessary feedstocks— H_2O , CO_2 , and H_2 . We investigate and compare four main CO_2 methanation pathways: thermochemical (via the Sabatier reaction), biochemical, photoelectrochemical, and electrochemical (Figure S1). By applying a standard discounted cash flow method to each technology, we assess the current status and future opportunities and compare different technology pathways side-by-side.

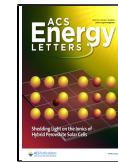
The detailed assumptions for the technoeconomic analysis (TEA) of technologies evaluated in this study are included in the Supporting Information, and the database files used for arriving at detailed cost values are also included in the Supporting Information. The baseline CH_4 production was assumed to be at a scale of 30 kton CH_4 /year (1,500 Mcf per year), or 81 ton CH_4 /day (4 Mcf/day). We calculate the CO_2 capture, H_2 production, and water generation rates needed to match this production rate, that is, H_2 production rate of 40 ton/day, CO_2 capture rate of 245 ton/day, and water generation rate of 365 ton/day. No carbon credits were accounted for in this study. The electricity price for all current systems was assumed to be \$49/MWh based on the 2018 data from solar utility PV in California.¹⁰ The TRL is evaluated from 1 to 9, where TRL 1–2 corresponds to the observation of basic principles in the academic development, TRL 3–4 to proof-of-concept development at lab scale, TRL 5–6 to process development and system integration from lab to prepilot scale, TRL 7–8 to optimization and precommercialization scale, and TRL 8–9 to commercial operation at scale.¹¹

The technological pathways considered in this study also included the traditional PtG routes, in which H_2 is produced via electrolysis followed by CH_4 synthesis.¹² In addition, while

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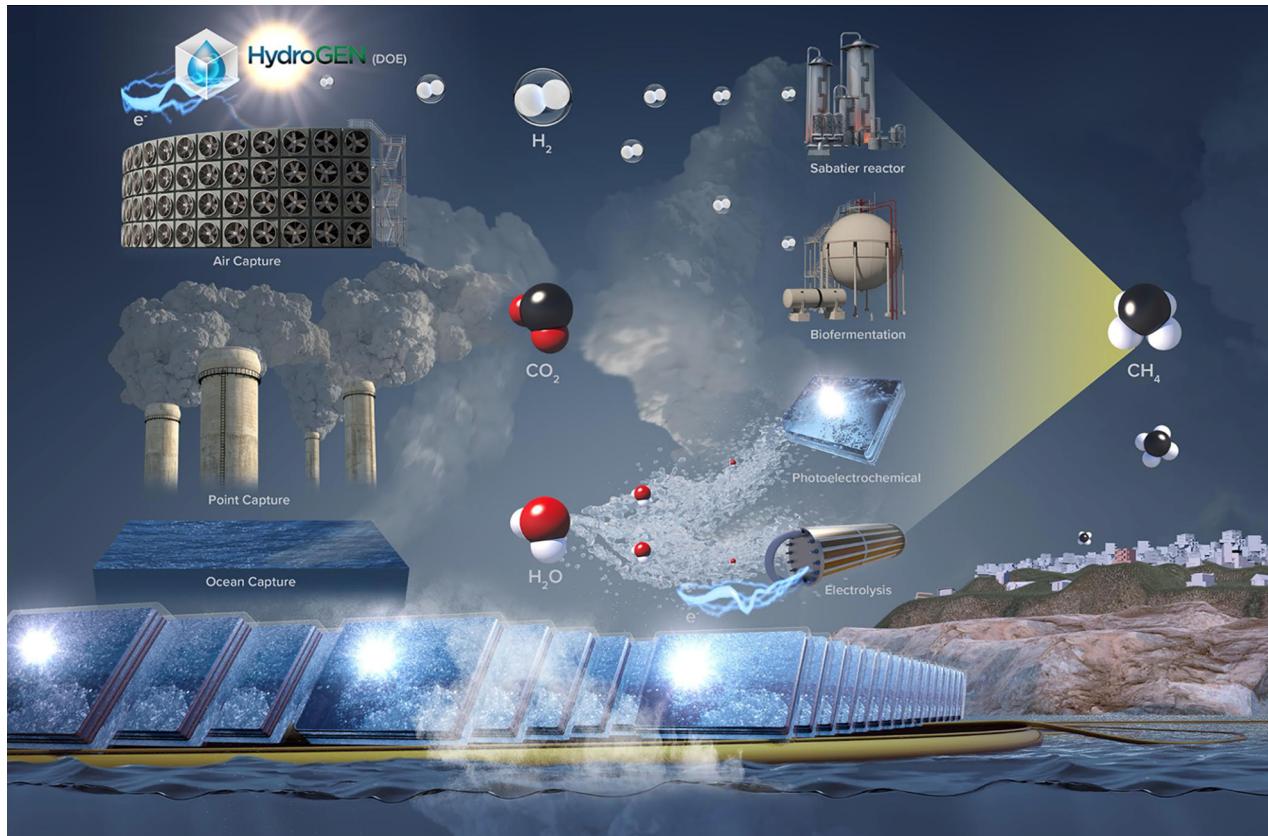


Figure 1. Schematic of various pathways to capture CO_2 , generate H_2 , and generate CH_4 from sunlight, H_2O , and sunlight.

many reports^{13–16} have focused on individual components of a renewable methane system, this work used the state-of-the-art performance metrics from specific technologies, including four advanced water-splitting technologies, CO_2 capture from air and ocean water, (photo)electrochemical CO_2 reduction into CH_4 , and thermo-chemical and biochemical methanation from H_2 and CO_2 , so that different technological pathways can be directly compared. Table 1 summarizes the cost estimate from this study, TRLs, and demonstrated scale for each technology, derived from literature reports of renewable generation of CH_4 .

Carbon dioxide can be captured from point sources of emission, atmospheric air, or ocean water. The location of capture often dictates where CH_4 generation can occur. CO_2 capture from point sources, such as oil refineries and the cement industry, is primarily based on chemical absorption and desorption of flue gas with amine solutions.^{17,18} Point source CO_2 capture was demonstrated at a rate of 20,000 ton/day by the Century NG plant in Texas in 2010.¹⁹ For a typical coal fired power plant, a CO_2 capture rate of ~5,000 ton/day provides a CO_2 emission reduction of ~10%.²⁰ Point source CO_2 capture utilizes relatively mature technology and has been validated by large industrial scale demonstrations at multiple locations, at an average TRL of 8–9. However, point source CO_2 capture is not compatible for a negative CO_2 emission future. A typical carbon capture system for a coal fired power plant reduces the plant energy efficiency, consuming 16% of the generated energy from the plant.²¹ Because point source capture has been deployed at large scale in multiple geographical locations, the estimated cost has converged to a narrow cost range of ~ \$60–70/ton CO_2 from reported literature.^{22,23}

Carbon dioxide can also be captured from the environment in a dilute form from either atmospheric air or from ocean water. Direct air capture (DAC) has been demonstrated at an early commercial scale.^{14,24} The operating principle of DAC from carbon engineering includes two sequential loops. In the first loop, CO_2 is captured from the atmosphere using capturing solvents, such as aqueous alkaline solutions, to form aqueous carbonate solutions. The second loop precipitates the carbonate using Ca^{2+} , regenerates the alkaline solution, and releases CO_2 by calcination.¹⁴ The largest system that is currently built based on this technology is capable of capturing roughly 1 ton CO_2 /day, which corresponds to a TRL of 7–8.¹⁴ Assuming 803 kWh/ton CO_2 to power calciner, compressor, pumps, etc. with the largest single line item being the air contactor, our TEA model predicts a cost of \$277/ton CO_2 at a plant capacity of 240 ton/day (Table S2). This is in good agreement with reported values.¹⁴ Assuming an energy input of 555 kWh/ton CO_2 and cost of electricity of \$10/MWh, we further estimate that the future cost for DAC can be reduced to \$115/ton, upon scaling to a plant capacity of 2,400 ton/day (Table S3).

Capturing CO_2 from ocean water is an attractive alternative to DAC because the concentration of CO_2 is 140 times higher in ocean water than it is in the air.¹⁶ The operating principle for ocean water capture is to shift the CO_2 /bicarbonate equilibrium toward dissolved CO_2 by acidifying ocean water, achieved via a process which lowers the pH of ocean water, such as electrodialysis. The acidified stream is then passed through a liquid–gas membrane contactor, which captures the gaseous CO_2 from the dissolved CO_2 in the aqueous stream. However, ocean water intake, pretreatment, and pumping from an offshore site to an onshore capture plant accounts for a

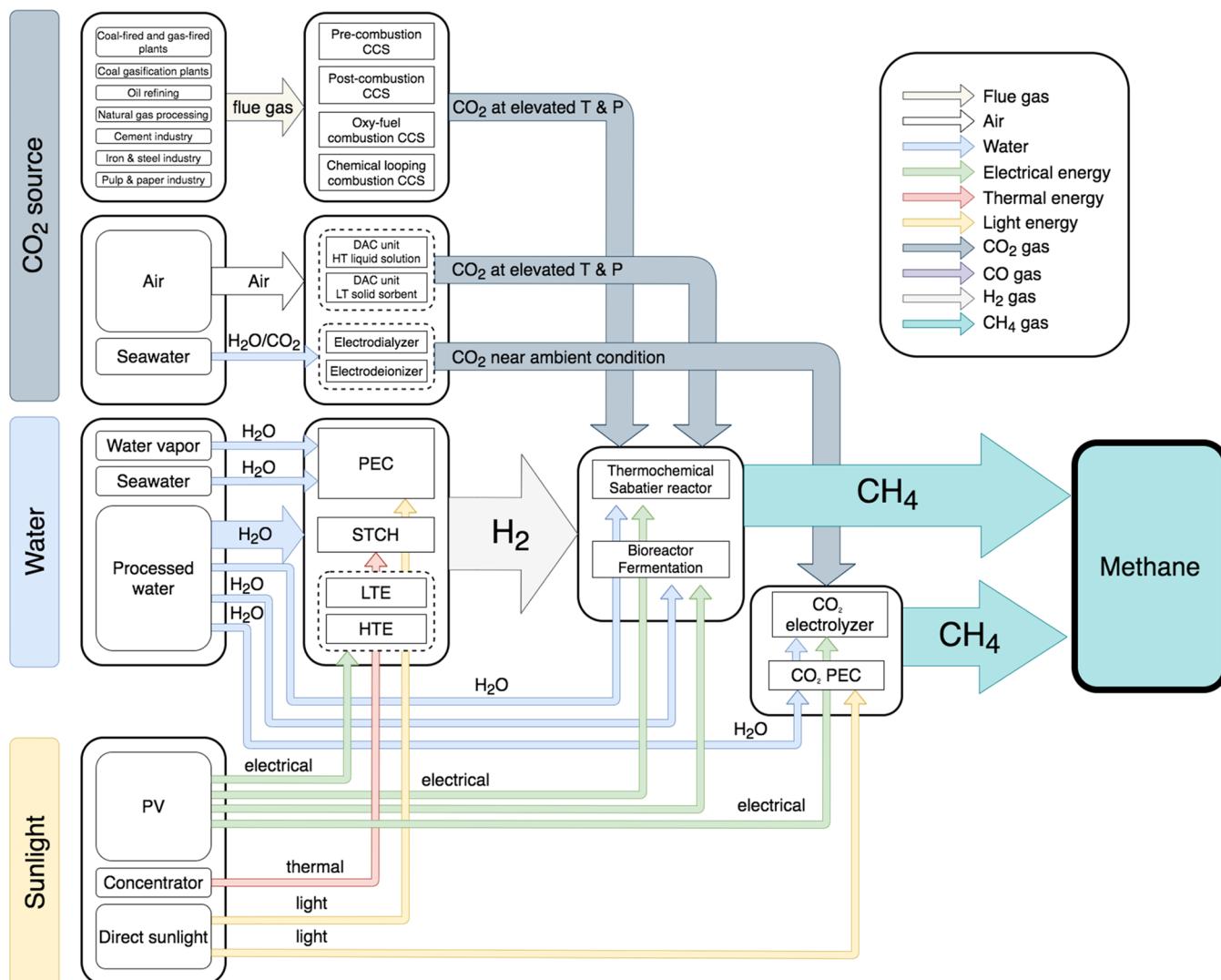


Figure 2. Schematic representation of various technology pathways for sustainable generation of methane from sunlight, water, and carbon dioxide.

major portion of the cost of capturing CO₂ from ocean water.¹⁶ By either colocating, with a desalination or electric power plant, or creating an onshore floating system, this cost can be significantly reduced.^{25,26} Electrochemical systems for the extraction of CO₂ from ocean water have been reported previously.^{16,27–30} Assuming current density of 100 mA/cm² and voltage of 1.2 V, we estimate the cost to be \$416/ton CO₂ for a floating CO₂ capture from ocean water system via electrodialysis with shallow intake and a plant capacity of 240 ton/day (Table S4). In the future, by assuming an increased system scale with throughput of 2,700 ton/day, electrodialyzer current density of 1 A/cm², and an electrodialyzer voltage of 1.6 V, the cost of the system can be reduced to ~\$118/ton CO₂ (Table S5). Our calculated current cost of \$402/ton of CO₂ for a floating ocean capture system is similar to the value reported by Eisaman et al.¹⁶ for a system that is colocated with a water desalination plant. Differences in assumptions made for electricity price, electrodialysis performance, pretreatment processes, and other economic assumptions account for the differences. While this technology appears to be promising, it is in its nascent phase, corresponding to a TRL of 5–6 for ocean water CO₂ capture given that the largest system realized to

date operates with a throughput of ~1 kg/day in a lab environment.³¹

Encouragingly, the costs for CO₂ capture from either air or ocean water via the most compelling processes may be able to reach <\$100/ton in the future. As CO₂ capture from dilute sources reaches this cost range, large-scale CO₂ utilization or storage will not be limited by the physical location of point sources of CO₂ emission. This will mark the transition to an infrastructure that can effectively offset CO₂ emissions from sources that are very difficult to address with a point-of-emission capture approach, such as consumer appliances and vehicles.

Regardless of the methanation technology used, water is required as a feedstock for the hydrogen content in CH₄. A small total amount of water is needed, and its cost is low, as compared to that of other steps in the process; thus, the choice of water generation method is largely dependent on the system location. Water can either be purchased at a utility scale, from a desalination plant, captured from the air with a membrane, or condensed out of the air by engineering desired thermal properties of the material.

Table 1. Summary of Cost, TRLs, and Demonstrated Scale of Different Technological Pathways for Renewable Generation of Methane^a

	Method	Current Cost \$/ton	TRL	Current demonstrated Scale
CO ₂ Capture	Point Source	60-70 ⁸¹	8-9	~20,000 ton/day ¹⁹
	Air	277 (115 in future)	7-8	~1 ton/day ¹⁴
	Ocean Water	416 (118 in future)	3-4	~1 kg/day ³¹
Water Source	Utility	<0.0003 ³²	8-9	~1.6 million ton/day ³³
	Desalination	1.62 ³⁵	8-9	~0.19 million ton/day ³⁵
	Membrane	150	8-9	~120 ton/day ⁴¹
H ₂ Generation	Condensation	339	5-6	~6 kg/day ⁴⁶
	Low Temperature Electrolysis (LTE)	3518	8-9	~2.6 ton/day ^{6,51}
	Photoelectrochemical (PEC)	5294	5-6	<1 kg/day ⁵⁸
	High Temperature Electrolysis (HTE)	3956	7-8	~1 ton/day ⁵⁶
CH ₄ Generation	Solar Thermochemical (STCH)	3706	5-6	<1 kg/day ⁶¹
	Electrochemical (2,500-10,000 with feedstock)	3-4	<1 kg/day ⁷²	
	Photoelectrochemical (1,500-17,000 with feedstock)	3-4	<1 kg/day ⁷⁵	
	199 without feedstock,			
	Thermochemical 2,797 with feedstock	7-8	~5 ton/day ⁶⁹	
	189 without feedstock,			
	Biochemical 2,830 with feedstock	7-8	~4 ton/day ⁶⁵	

^aThe cost of methane generation in the thermochemical and biochemical routes assumed water from utility, CO₂ from direct air capture, and H₂ from LTE as the feedstock.

Utility-scale water is the cheapest option because of its scale and government subsidy. The price of groundwater depends on the pumping depth, energy source, cost of energy, and the amount of water available. Prices in 2010, according to the Organization for Economic Cooperation and Development (OECD), range from \$0.000195/ton in California to \$0.00023/ton in Arizona.³² For our analysis, we used the water cost in California. One of the largest water suppliers is the Los Angeles Department of Water and Power (LADWP), which supplied 632 billion liters of water in 2014.³³ Another water generation option is desalination, in which ocean water is processed with a pretreatment filter to remove large particles and is then forced under high pressure through a membrane to perform reverse osmosis. The fresh water is then treated for drinking, and the brine is discharged to the ocean.³⁴ Large-scale desalination has been demonstrated only at a tenth of the scale of utility water sources. For example, in 2015 San Diego deployed a desalination plant that produces 68.9 billion liters of fresh water per year at a cost of \$1.62/ton.³⁵ While more expensive, water supply from desalination is preferable in locations near the ocean with minimal rainfall. Both of these technologies are assigned a TRL of 8–9 because of their large scale and multiple plant locations.

Alternative routes for water generation involve extraction from atmospheric air. While these methods are more expensive and have lower TRLs, they remove location restrictions for CH₄ production systems. One way to extract water from the air is via a membrane or mesh, which provides a surface upon which water vapor in the atmosphere can condense. These droplets are harvested into a collection area under the influence of gravity drop.³⁶ This has been shown in numerous

studies^{37–39} and demonstrated on a larger scale at 12 ton/day.⁴⁰ We assign a TRL of 8–9 for the membrane water-capturing technology.⁴¹ The cost of water obtained from membrane capture is estimated to be \$60/ton at a plant capacity of 365 ton/day (Table S6). Another way to remove water from the air is by using radiatively cooled surfaces to condense water out of the air.^{42–45} In these systems, materials are designed to maximize infrared emission properties and allow the surface to be cooler than ambient temperature. This change in temperature between surface and ambient air promotes the condensation of atmospheric water on the surface, which can then be harvested.³⁶ Currently, condensation via radiative cooling is the most expensive option among those we considered, because of the high capital expense for purchase of the materials to capture water at a relevant scale. The largest demonstration to date is by OPUR (International Organization for the Utilization of Dew), which has shown a system that can generate 0.006 ton/day, which we assign a TRL of 5–6.^{45,46} We estimate the cost of water using radiative cooling to be \$339/ton at a scale of 365 ton/day (Table S7).

Despite the significant cost differences between various water generation strategies, the cost of water remains lower than other costs of a renewable methanation system. For low-temperature electrolysis, if water produced via membrane air capture is used rather than utility water, the cost of hydrogen increases from \$3.48/kg to \$4.53/kg. It is notable that no matter where a methane system is deployed—near a utility water source, an ocean, or in the desert—that generating water is likely not to be a limiting factor.

CO₂ and water are the main raw feedstocks for direct methanation pathways (electrochemical and photoelectro-

chemical); however, indirect methanation pathways (thermochemical and biomethanation) (Figure 2) rely on reaction between CO₂ and H₂. It is therefore appropriate to assess the technology options for renewable H₂ generation from water. The renewable generation of H₂ is also the most critical step in all the PtG studies.^{6,12,47–49} We focus on four H₂ generation technologies, including low-temperature electrolysis (LTE), photoelectrochemical (PEC), high-temperature electrolysis (HTE), and solar thermo-chemical (STCH). We used H2A analyses guidelines and applied the DOE financial and operational assumptions that are adjusted to our case studies to calculate the cost of hydrogen generated using these technologies.⁵⁰ All technologies are evaluated at a design capacity of 40–45 ton H₂/day. This average production will therefore maintain the 81 ton CH₄/day (4 Mcf CH₄/day) production required by our baseline assumptions.

The largest scale demonstrated for LTE thus far is 10 MW, corresponding to ~2.6 ton/day generation rate.⁵¹ MW-scale LTE systems were also deployed worldwide, at an average TRL of 8–9.⁵² In LTE, H₂ is produced at the cathode and O₂ at the anode electrochemically under a voltage bias. The cathode and anode are separated by a membrane separator.⁵³ Three types of LTE systems have been developed, including alkaline water electrolysis, proton exchange membrane-based water electrolysis, and hydroxide exchange membrane-based water electrolysis.⁵⁴ State-of-the-art proton exchange membrane (PEM) cells operate at ~2 A cm⁻² and ~2 V with a stack level efficiency of 55 kWh/kg of H₂.⁵⁴ We assume an operating voltage of 1.9 V/cell, current density of 2 A/cm², and stack life of 7 years.^{15,50} From this we estimate the current cost of a PEM system at a design capacity of 40 ton/day is \$3,518/ton (Table S8). The values that we calculated are similar to those calculated previously but significantly lower than those calculated by the Department of Energy (DOE) case study.¹⁵ The discrepancy was largely due to the higher cost of electricity assumed by the DOE of \$87/MWh and the higher after-tax real internal rate of return (IRR) of 8%.^{50,55} A sensitivity analysis (Figure S1) for the impact of electricity cost, energy efficiency, capital expenditures (CapEx), and after-tax real IRR on the cost of hydrogen indicates that presently the electricity cost was the largest lever among those variables.

High-temperature electrolysis (HTE) is another H₂ production method using electricity. The operating principle for HTE is very similar to LTE. High-temperature electrolysis cells include a cathode for water reduction, an anode for oxygen generation, and a solid ceramic material, which is used as the electrolyte to selectively conduct oxygen ions (O²⁻) at ~700°–800 °C.⁵⁵ It has been demonstrated at a scale of 2.6 MW, corresponding to ~1 ton H₂/day.⁵⁶ Assuming an energy usage of 51 kWh/kg H₂,⁵² we estimate the cost of the HTE system to be \$3956/ton H₂ (Table S9), which was similarly less than the value calculated by the DOE (\$4,660/ton).⁵⁰ Both LTE and HTE use electricity for H₂ generation; as a result, the electricity price has a large influence on the cost of H₂ from both technologies. For instance, at a scale of 40 ton H₂/day, the LTE system will produce H₂ at \$2,410/ton with an electricity price of \$30/MWh, whereas at an electricity price of \$60/MWh, the cost of H₂ is \$4,160/ton.

Photoelectrochemical (PEC) and solar thermochemical processes (STCH) produce H₂ from sunlight and water. Photoelectrochemical water-splitting cells integrate multiple functional materials and couple water oxidation and hydrogen evolution reactions to produce molecular hydrogen and

oxygen. Key PEC processes include light absorption, photo-generated carrier transport, electrocatalysis, ionic transport, and product separation.⁵⁷ Photoelectrochemical devices operate at much lower current densities, typically in the range of ~10–100 mA cm⁻², relative to LTE or HTE, because the production rate is matched to the solar flux. State-of-the-art PEC devices have exhibited a solar-to-hydrogen conversion efficiency of 19.3%.⁵⁸ Currently, PEC devices have been demonstrated only at a laboratory scale of <1 kg/day H₂, giving it a TRL of 5–6.¹³ Assuming a solar-to-hydrogen (STH) efficiency of 10%, photovoltaic (PV) efficiency of 19.1%, cost per unit area of \$161/m² (which includes the cost of PV cells, catalyst, membrane, chassis, water processing, gas processing, power electronics, and control system),¹³ the current cost of H₂ from PEC is estimated to be \$5,294/ton (Table S10). However, the projected price drops of photovoltaic materials, dramatic improvements in membrane costs, and increases in solar-to-fuel efficiency are projected to lead to a significantly reduced cost for H₂. For example, with an STH efficiency of 20%, PV efficiency of 25%, and cost per unit area of \$119/m² (which includes the cost of PV cells, catalyst, membrane, chassis, water processing, gas processing, power electronics, and control system), we estimate the cost of PEC H₂ can reach \$1,775/ton in the future (Figure S2 and Table S11). The estimated value is lower than values calculated by Shaner et al.,¹³ because of a higher assumed solar capacity factor of 28.4% (for California) in our case study, as opposed to 20%, and a more up-to-date value of \$0.37/W⁵⁹ for the cost/Watt of photovoltaic panels (see the Supporting Information).

Solar thermochemical (STCH) cycles use the heat from sunlight to produce hydrogen and oxygen from water. STCH uses two-step redox active metal oxide thermochemical cycles to produce H₂ and O₂ sequentially in two different chemical reactions.⁶⁰ STCH has been demonstrated at ~1 kg/day, giving it a TRL of 5–6.⁶¹ Using an economic model adapted from the U.S. DOE H2A analysis,^{50,62} assuming an STH efficiency of 20% and plant capacity factor of 90%, we estimated H₂ cost from STCH to be \$3,706/ton for a system with a design capacity of 45 ton H₂/day (Table S12).

H₂ generation is the largest cost driver for indirect renewable CH₄ generation and is expected to play a critical role in a broader setting in future energy systems. However, it is important to realize that presently the largest demonstrated H₂ generation project even with the highest TRL technology, that is, low-temperature electrolysis, is limited at <3 ton of H₂ per day. Note that a single digester colocated with a dairy farm produces on average ~5 ton of CH₄ per day, which translates to ~2.5 ton H₂/day required based on the CO₂ methanation reaction. Hence, it is not surprising to note that large electrolysis projects for renewable generation of H₂, such as a 156 ton H₂/day system in France,⁶³ have been planned in the near future.⁶ However, converting H₂ to CH₄ has its own advantages. CH₄ has ~3.5 times higher storage capacity than H₂, and H₂ is significantly more difficult to store because it is corrosive and leads to embrittlement of container materials.⁶⁴ Considering this last point, many costly modifications and component replacements would be needed in the legacy gas piping, storage, and distribution infrastructure to make it compatible with H₂ distribution rather than methane distribution. These infrastructure utilization considerations represent a strong argument in favor of renewable methane as an alternative to H₂, as a gas energy carrier for widespread distribution.

Having surveyed pathways to generate the raw feedstocks needed for renewable methane synthesis, we now analyze and compare different methanation pathways. We separate these into two main categories: (i) indirect CO₂-to-CH₄ conversion via thermochemical and biomethanation methods and (ii) direct CO₂-to-methane conversion via electrochemical and PEC methods.

The two indirect methane conversion methods that we focus on are thermochemical methanation via the Sabatier reaction and biochemical methanation. Biochemical methanation has been demonstrated at 5 MW scale, or ~4.3 ton/day from Electrochaea.⁶⁵ We assign a TRL of 7–8 for this technology. The basic technology relies on anaerobic microorganisms called methanogenic archaea that are able under certain conditions to produce CH₄ from H₂ and CO₂ with high selectivity.⁶⁶ These organisms exist naturally in the environment and have been selectively evolved for higher selectivity in these reactors. In this process, the archaea are heated up to 60 °C and pressurized to ~10 bar and then fed CO₂ and H₂.⁶⁵ The organisms can then self-sustain the heat and highly selectively convert the CO₂ and H₂ to CH₄. Assuming a 99% efficient biological methanation reactor,⁶⁵ biochemically produced CH₄ is estimated to have a cost of \$189/ton without the feedstock cost and \$2,830/ton (Table S13) assuming that the H₂ is generated via LTE and the CO₂ is captured from air.⁶⁷

We focus on the Sabatier reaction as a method for thermochemical methanation. Similar to the biomethanation route, CO₂ is reacted with H₂; however, instead of using a micro-organism the reactor is heated to ~350 °C in the presence of a catalyst (i.e., Ni). The CO₂ and H₂ then react exothermically to produce CH₄.⁶⁸ The largest Sabatier reactor built thus far is a 6 MW reactor by Audi at their Audi e-gas facility in Germany.⁶⁹ We estimate a TRL of 7–8 for this technology. Assuming a conversion efficiency of 93%, we calculate the cost of thermochemical methanation to be \$193/ton CH₄ without the feedstock cost and \$2,791/ton CH₄ (Table S14) using H₂ generated via LTE and CO₂ captured from air.

Figure 3 shows the cost breakdown for the indirect methanation methods, assuming H₂ generated via PEM electrolysis, CO₂ captured from the atmosphere, and H₂O from a utility source. The cost for CO₂ capture and the methanation process (both thermochemical and biochemical) are small, and it is clear that the cost of renewable H₂ generation is the largest cost component for the indirect methanation pathways. As shown in Figures 3 and Figure S1, the cost of electricity remains the largest cost and largest lever for renewable H₂ generation via LTE, which is consistent with recent DOE reports.⁶²

For the direct methane conversion methods, we first consider an electrochemical system powered by grid electricity at a high-capacity factor, similar to LTE H₂ electrolysis. The main differences between an H₂ electrolysis and a CO₂ electrochemical system comes from the consideration of charge transfer in electrocatalysis, which requires 8 electrons per CH₄ molecule from CO₂ as opposed to the 2 electrons needed for generation of an H₂ molecule. Currently, the multielectron and proton reaction still faces significant challenges in selectivity, activity, and durability.^{70,71} One of the highest-performing electrolysis systems developed exhibited a Faradaic efficiency (FE) of 85% for CH₄ generation with an overpotential of 2.8 V at ~25 mA/cm².⁷² Electro-

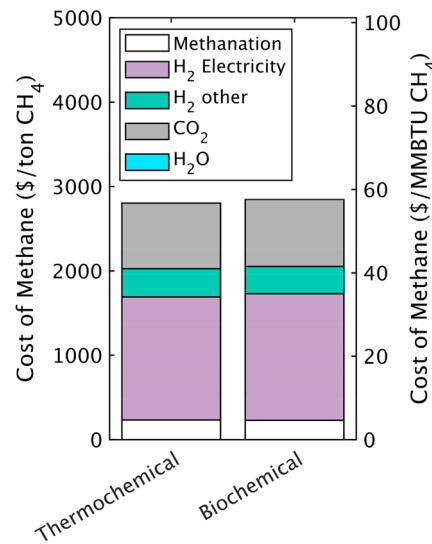


Figure 3. Cost breakdown of the green methane from thermochemical and biochemical processes. The feedstock of the thermochemical and biochemical process assumed water from utility, CO₂ from direct air capture, and H₂ from LTE with an electricity price of \$49/MWh.

chemical CO₂ conversion devices have also exhibited high operating current densities up to 700 mA/cm² in other reduction products such as CO and ethylene.^{73,74} The cost for the direct electrochemical methanation process as a function of the operating current density and the energy efficiency of the cell is illustrated in Figure 4a. A range of operating current density from 10 mA/cm² to 5 A/cm² and a range of Faradaic efficiency from 50% to 100% were considered for the direct electrochemical CH₄ generation. Note that the overall cell efficiency is a combination of the Faradaic efficiency of the reaction and the operating cell voltage. At an operating current density of 100 mA/cm² and an energy efficiency of 15%, the cost of CH₄ was estimated to be \$10,700/ton CH₄ (Table S15), assuming \$278/ton CO₂ captured from the atmosphere and a plant size of 81 ton/day. If we assume a more optimistic device performance of 5 A/cm² and an energy efficiency of 56%, the cost of CH₄ was estimated to be \$2,420/ton CH₄ (Table S15), assuming \$278/ton CO₂ captured from the atmosphere and a plant size of 81 ton/day. Considering the demonstrated current density and energy efficiency in the literature, the electrochemical methanation is not competitive with indirect methanation techniques. It would require very significant advancement in materials and device development to be cost competitive with the indirect methanation processes.

Photoelectrochemical (PEC) methanation operates using the similar mechanisms as PEC H₂ generation except that the electrons are reducing CO₂ instead of H₂O. Both PEC H₂ and PEC methanation use water as the proton source. Photoelectrochemical methanation also faces similar challenges as the electrochemical methanation, specifically the fact that producing methane requires 8 electrons, and because PEC devices are limited by the solar flux, this limits the rate of methanation. A PEC methanation device has been realized with a solar-to-fuel efficiency (STF) of 0.1%.⁷⁵ While PEC methanation has significant challenges in the activity and selectivity, other PEC CO₂ reduction devices, such as CO₂ reduction to CO or formate, have reached STF conversion efficiency of >10%.⁷⁶ The cost for a direct PEC methanation

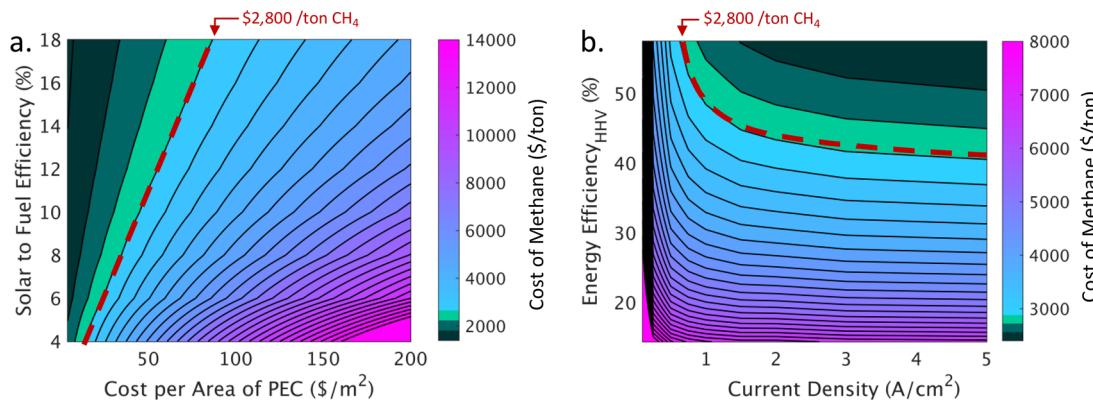


Figure 4. Cost of methane from (a) photoelectrochemical (PEC) and (b) electrochemical methanation processes as a function of key performance metrics in those technologies. (a) The cost of PEC methanation as a function of the STF conversion efficiency and the cost per area of PEC material. (b) The cost of electrochemical methanation as a function of the energy efficiency of the device and the operating current density. The green region in both plots shows where the cost is equal to or less than thermochemical or biochemical methanation. The cost of CO₂ is assumed to be \$278/ton and the electricity price is \$49/MWh for the systems compared.

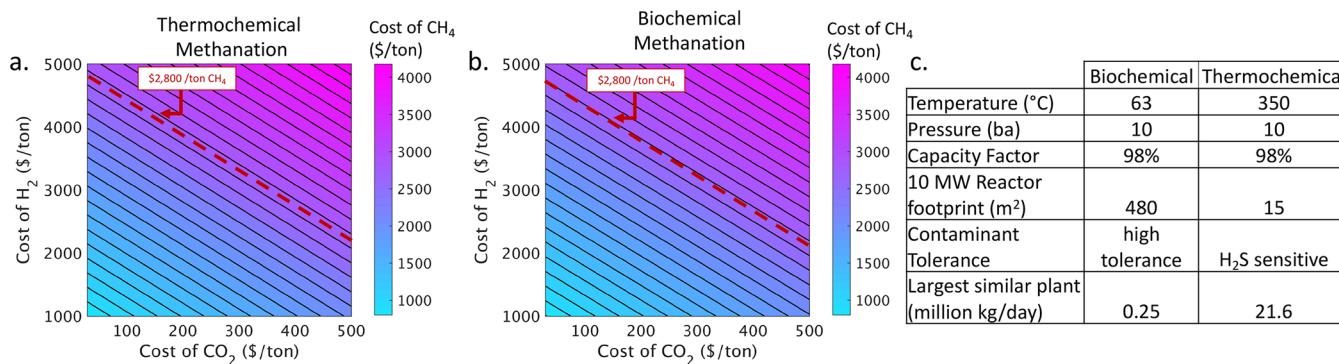


Figure 5. Cost of the (a) thermochemical and (b) biochemical methanation processes as a function of H₂ cost and CO₂ cost. (c) Side-by-side comparison between the biochemical methanation process and the thermochemical methanation process.

pathway as a function of the cost per area and the STF conversion efficiency is illustrated in Figure 4b. A range of STF conversion efficiency from 4% to 18% was considered for direct PEC CH₄ generation. At an STF of 4% for the PEC methanation device, and a \$200/m² constructed in a PEC type 3 configuration,¹³ we estimate the cost of CH₄ to be to be \$16,930/ton (Table S16). If we assume more optimistic device metrics of an STF of 18% for the PEC methanation device, and a \$10/m² constructed in a PEC type 3 configuration,¹³ we estimate the cost of CH₄ to be to be \$1,500/ton (Table S16). As shown in Figure 3b, for PEC methanation to be competitive with indirect methanation, the cost of the system per square meter must be significantly reduced in addition to improvements in efficiency.

Panels a and b of Figure 5 show how the cost of thermochemical and biochemical methanation is affected by the cost of the feedstocks. The cost of both approaches is very close because of the similarity of their CapEx's and that the CapEx makes up 75% of the methanation cost. The CapEx's are similar because much of the equipment required for both systems is the same, that is, items such as compressors, reactor, pumps, piping, etc. The heterogeneous catalysts in the thermochemical methanation and the anaerobic microorganisms in the biochemical methanation were not the main cost driver for methanation. Other factors to consider are listed in Figure 5c. One advantage of biochemical methanation is its high tolerance for contaminants, whereas catalysts for the

Sabatier reaction are highly sensitive to H₂S.^{48,77} This advantage is most important when the CO₂ is being captured from point sources; however, CO₂ captured from the air or ocean water environment is likely to result in a very pure CO₂ stream, making this difference less important. Another advantage of biochemical methanation is the lower operating temperature, making it possibly more suitable for small-scale reactors.^{65,78} However, thermochemical methanation may be favorable when considering scaling of methanation to a large capacity. First, the required areal footprint of the reactor is significantly smaller.^{49,67,79} Second, from examination of scales of similar processes for biochemical and thermochemical such as Fischer-Tropsch via thermochemical or bio ethanol for biochemical methanation, there is nearly a 100× difference in scale at which these processes have been demonstrated, suggesting it may be significantly easier to scale up thermochemical methanation than biochemical methanation.

In summary, thermochemical or biochemical methane generation using CO₂ captured from point sources and H₂ produced from low-temperature electrolysis powered by renewables turned out to be the most cost competitive pathway in the short term. The cost of renewable H₂ is found to be the dominant cost component of renewable methane synthesized by indirect methanation. We also found that the cost of CO₂ from dilute sources (air or ocean water) is likely to be competitive with CO₂ from point sources as the technology advances, and the cost of CO₂ will not be a cost driver for CH₄.

generation. The largest demonstrated scale for direct CO₂ capture from air (~1 ton CO₂/day), the renewable H₂ generation via low-temperature electrolysis (~2.6 ton H₂/day), the thermo-chemical methanation (~5 ton CH₄/day), and the biochemical methanation (~4 ton CH₄/day) are all very small and are dwarfed by a single anaerobic digester colocated with a dairy farm. As the cost of the renewable electricity continues to decrease, at an electricity price of \$10/MWh, we estimate that an overall optimistic cost of \$983/ton of CH₄ in the future, which is then cost competitive to the market CH₄ price in certain regions of the world,⁸⁰ can be achieved. In the long term, significant improvements of key performance metrics in electrochemical and photoelectrochemical methanation can provide unique alternatives to the short-term pathway winners with more energy resilience and ultimately achieve CH₄ production cost of <\$1,000/ton.

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■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenergylett.1c00174>.

Analytical Basis, Supplementary Tables S1–S16, and Supplementary Figures S1–S5 ([PDF](#))

Excel spreadsheets: Biochemical Methanation, Condensation Water Capture, Direct Air Capture of CO₂ (current), Direct Air Capture of CO₂ (future), High Temperature Electrolysis H₂, Low Temperature Electrochemical CH₄, Low Temperature Electrolysis H₂, Membrane Water Capture, Ocean CO₂ Capture (current), Ocean CO₂ Capture (future), Photoelectrochemical CH₄, Photoelectrochemical H₂ (current), Photoelectrochemical H₂ (future), Solar Thermochemical H₂, and Thermochemical CH₄ ([ZIP](#))

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Author Contributions

§A.J.W. and I.A.D. contributed equally to this work. A.J.W., I.A.D., R.K., P.G., C.X., and H.A.A. conceived the idea and examined the feasibility of such a process. A.J.W. and I.A.D. performed all of the calculations and research required to complete the energy analysis of various systems. R.K., P.G., C.X., and H.A.A advised throughout the process and provided valuable input for determining the viability of various proposed processes. A.J.W., I.A.D., C.X., and H.A.A. wrote the paper, and all authors commented on the manuscript.

Notes

Views expressed in this Energy Focus are those of the authors and not necessarily the views of the ACS.

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