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Economically Advantageous Pathways for Reducing Greenhouse Gas Emissions from Industrial Hydrogen under Common, Current Economic Conditions

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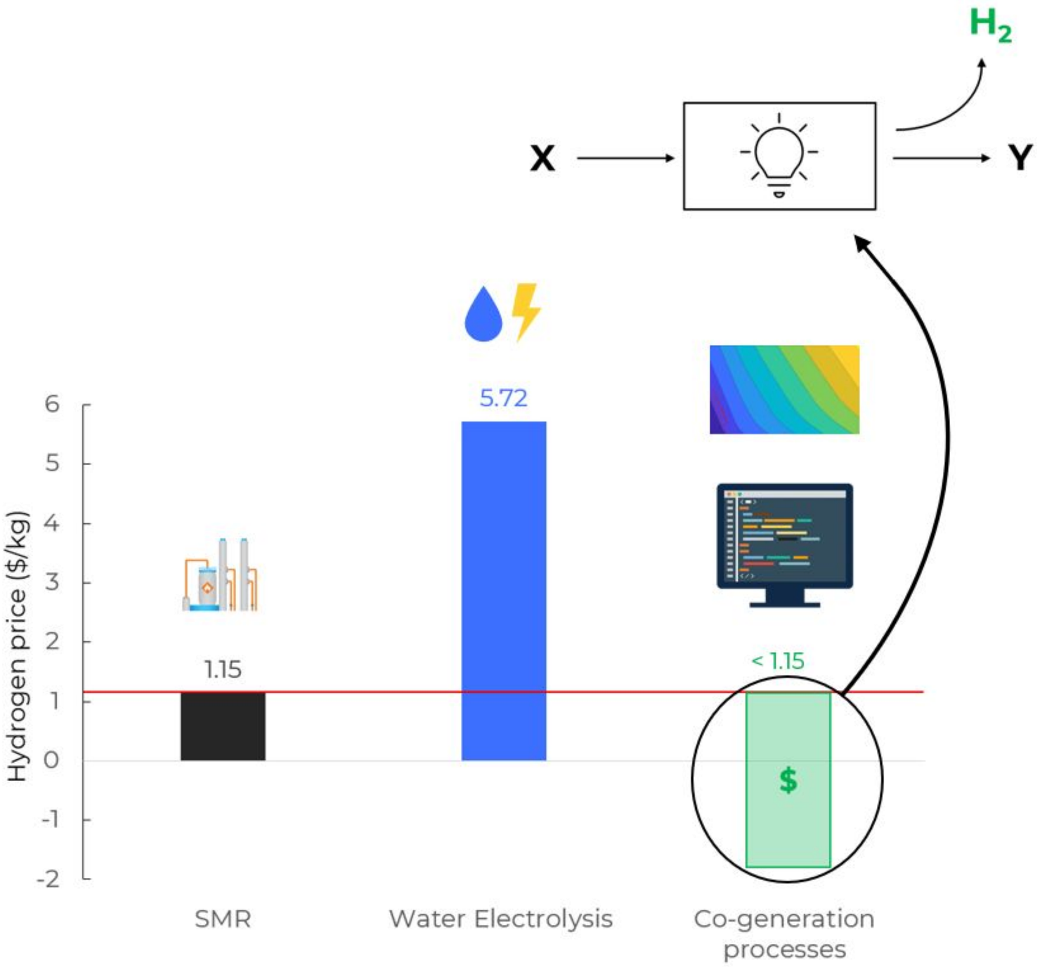
Abstract

Hydrogen is a major industrial chemical whose manufacture is responsible for ~3% of global carbon dioxide emissions. >95% of hydrogen is made via reforming fossil fuels which typically co-produces hydrogen and waste carbon dioxide. Nearly all other hydrogen is co-produced with other commodity chemicals. Unfortunately, many alternative, clean hydrogen production processes are small-scale because they require major reductions in capital cost or energy prices to be economical enough for industry. Because the climate problem is urgent, and the economics of future energy is uncertain, this paper seeks to expand the options for producing industrial-scale, clean hydrogen under common, present-day economic conditions. First, we build a model to understand the economic and carbon dioxide emissions constraints of sulfur electrolysis which is an emerging process that cogenerates hydrogen and co-salable sulfuric acid and has the potential to produce up to 36% of the world's current hydrogen demand under present-day, average US economic conditions. We also use our model to evaluate water electrolysis, which cogenerates hydrogen and waste oxygen, but is not economical under present-day average US economic conditions. We then propose criteria for identifying clean hydrogen production chemistries. Using these criteria, we find enough reactions to have the combined potential to make over 150% of the world's industrial hydrogen needs under present day average US economic conditions while reducing cost and reducing or eliminating CO_2 emissions. Given the urgency of the climate problem, we believe that an economic analysis, such as this is crucial to near term CO_2 emissions reductions.



Broader Context

Industrial processes are responsible for over 30% of global greenhouse gas emissions[1]. The "big 4" industrial emissions sources are the production of cement, steel, hydrogen, and aluminum which, combined, account for almost 16% of global GHG emissions[1,2]. Hydrogen production alone is responsible for over 2% of global greenhouse gas emissions, approximately the same as all of the world's airplanes[1,3].

The problem with decarbonizing the hydrogen industry is a problem of cost. Despite decades of development in currently high-cost alternative hydrogen production pathways like water electrolysis, methane pyrolysis, and biomass gasification, the low-cost, CO_2-intensive steam reforming fossil fuels still accounts for >95% of global hydrogen production. Meanwhile, ultra-low-cost technologies like plasma cracking methane have gone from lab to industrial scale in less than a decade[4]. One of the key examples of slow adoption and high cost is water electrolysis which even after over 200 years of development has minimal market share and is well-known to be 4-10X more costly than steam-reforming fossil fuels under modern economic conditions[5–8]. In this paper, we present novel chemistries that may be able to quickly replace the emissions-intensive steam reforming of fossil fuels and meet the world's hydrogen demand because they are both clean and low cost.

Introduction

Hydrogen is among the most consumed chemicals on the planet by mol (~35 teramoles/year; 74 MMT/year)[5,9–11]. It is used primarily (~49%) for the production of ammonia and the hydrodesulfurization of petrochemicals (~37%)[5]. Currently, >95% of hydrogen is made from the thermochemical reformation of fossil fuels. Hydrogen production is responsible for ~3% of global CO_2 emissions annually, equal to the overall emissions of airplanes (~2.25% of greenhouse gas emissions; ~1,200 MMT of CO_2 per year) [1,5]. The most common hydrogen production process, Steam Methane Reforming (SMR), may co-produce hydrogen with CO_2 for ~$1.15 per kg hydrogen in the US[6,7]. SMR CO_2 is typically wasted but also may be used in the synthesis of urea fertilizer or for enhanced oil recovery[12]. Some hydrocarbon reformation reactions may also cogenerate process-emissions-free, low-cost hydrogen. One such emerging technology is plasma cracking methane which since 2012 has demonstrated the potential to make industrial scale, market-rate, process-emissions-free hydrogen from natural gas as a co-generation product to carbon black[4]. The market for carbon black is ~1.2 Tmol/year (14 MMT carbon black/year) meaning that, at full scale, plasma cracking could produce ~7% of the world's hydrogen demand at a 2:1 H_2:C molar ratio (7 MMT H_2/year)[13]. Another example of clean hydrogen from fossil carbon reformation is steam cracking propane to make propylene which produces ~3 Tmol hydrogen per year (6 MMT H_2/year ~8% of global demand) without co-generating CO_2. This hydrogen is so cheap that it is usually burned for heat, but in some modern refineries it is separated and utilized for hydrodesulfurization[14]. The major technology, besides the reformation of hydrocarbons, that has produced hydrogen at the industrial scale is the Chlor-Alkali Process which currently produces ~0.75 Tmols of hydrogen per year (1.5 MMT H_2/year, ~2% of global demand)[15]. Older chlor-alkali plants oxidize this hydrogen for electricity, but modern plants sell it at market rate[10,16]. The total combined theoretical, economical process-emissions-free hydrogen production capacity of plasma cracking methane, steam cracking propane, and the chlor-alkali process is therefore ~5.25 Tmols/year (12.5 MMT H_2/year) or ~17%

of current hydrogen demand. Unfortunately, much of this process-emissions-free hydrogen is unutilized, likely due to the low economic benefit of retrofitting fully depreciated, outdated infrastructure[16].

While these cogenerative technologies show great promise in the near term, there are many technologies that as of 2020 are relatively unused and are also not estimated to produce hydrogen for \$1.15 per kg under current economic conditions. These so-far relatively small scale hydrogen production technologies include water electrolysis (co-produces hydrogen and oxygen gas), various thermochemical water splitting cycles (co-produces hydrogen and oxygen gas)[17,18], biomass gasification (co-produces hydrogen and CO_2), and methane pyrolysis (co-produces hydrogen and solid carbon) which are estimated to produce hydrogen for ~\$5.50 (380% more than SMR)[5–7], ~\$4 (250% more than SMR)[19], ~\$2.41 (110% more than SMR)[6], and ~\$1.58 (40% more than SMR)[20] per kg hydrogen respectively. We also acknowledge that there are many individual locations where these prices are lower, some notable examples for water electrolysis which may yield prices as low at \$2.93/kg H_2 are Texas, USA and Germany where there are renewable electricity subsides in excess of \$.023/kWh[21], or Quebec, Canada which has near 100% capacity factor mixed hydro and wind electricity for \$0.024/kWh (compared to average US electricity at \$0.07/kWh)[2223], or places with high capacity, low cost solar energy[24].

In the present analysis, we seek to understand the economics governing the production of clean hydrogen. We begin by modeling the economics of Sulfur Electrolysis (SE), an emerging electrochemical process which cogenerates hydrogen and sulfuric acid at a 1:1 molar ratio and could cogenerate ~3.25 Tmols/year of clean hydrogen (~9% of global hydrogen demand) if it met the global demand for sulfuric acid[25]. Additionally, cogeneration of these commodities may be especially valuable because sulfuric acid and hydrogen are commonly co-consumed in fertilizer production processes[26]. Future SE technology may electrolyze H_2S (a byproduct of oil and gas mining or, in a fossil-fuel-free future, a byproduct of mining sulfur and sulfide minerals like some copper ores) thus producing hydrogen and sulfuric acid at a 4:1 molar ratio which could provide 36% of the world's hydrogen demand and therefore may eliminate the need for SMR at ammonia plants.

We then use this model to compare the economics and emissions intensity of SE to the more well-studied water electrolysis (WE). One key economic assumption that we explore in this comparison is what it would take for hydrogen produced from ultra-low-cost, intermittent solar to be cheaper than hydrogen made on grid electricity. Finally, we define criteria for finding economically advantageous, process-emissions-free hydrogen production pathways. Given the projected urgency of reducing greenhouse gas emissions, we consider it imperative to create near-term models to find economically efficient pathways to reduce CO_2 emissions from hydrogen production[13].

Methods

Our model uses current component Capital Expenditure (CapEx) and Operating Expenditure (OpEx) values from the DOE H2A model and it takes a set of empirical data that represents allowed operational parameters (voltage, current, maximum capacity factor, etc) and then calculates the optimized cost of hydrogen given those inputs. Our model defines the CapEx for major plant components including, the electrolyzer, the AC/DC rectifier, the DC/DC converter, batteries, photovoltaic cells (PV), the hydrogen compressor, and in the case of SE the sulfuric acid concentrator and the SO_2 generator. Other components are treated as the balance of systems (e.g. land, wiring, owner's fees, installation labor, and piping). The model also includes routine maintenance, major maintenance, labor, and raw materials (e.g. water, electricity, and for SE, sulfur). The model assumes that operational parameters (e.g. operating voltage, current density, and faradaic efficiency) and CapEx at various plant sizes are governed by a set of empirical scaling relationships (Eqs S1-S7). As in the H2A model, electrochemical components scale stepwise in 500 kg H_2/day increments[6,7]. Other active systems (e.g. SO_2 generator and sulfuric acid concentrator for SE) scale non-linearly according to empirical data from these systems in the real world. The electrolyzer's operational parameters are governed by demonstrated experimental evidence (see sections below). Table 1 shows many CapEx and OpEx parameters for this model, and a full list may be found in table S3. All model code can be found in the supplemental materials.

Table 1. Plant OpEx and CapEx data in 2020 USD.

CapEx	
Electrolyzer Size (in kg H_2/day)	500
Water Electrolyzer ($\$10^3$/electrolyzer)[a]	532
Sulfur Electrolyzer (at 1.2 A/cm^2; $\$10^3$/electrolyzer)	632
Electrolyzer Hard BoS ($\$10^3$/electrolyzer)	600
DCDC converter ($\$10^3$/electrolyzer)	471
Installation ($\$10^3$/electrolyzer)	136
Soft Balance of Systems ($\$10^3$/electrolyzer)	24
OpEx	

PEM Electrolyzer Electricity Consumption (kWh/kg H_2)	49
Balance of Systems Energy Consumption (kWh/kg H2)	5
Electricity from Sulfur Burning (kWh/kg H_2)	12
Sulfur Electrolyzer Energy Consumption (kWh/kg H_2)	33
Routine Maintenance (% of install CapEx/year)	3
Major Maintenance (% of install CapEx/7 years)	15

Note. [a]Reference case.

Detailed Model Description for Sulfur Electrolysis

The primary steps of SE (equations 1 and 2) have been investigated extensively because equation (1) is the first step in the Contact Process (the standard thermochemical process to produce sulfuric acid)[27] and equation (2) is the electrochemical step in the Hybrid Sulfur Cycle (a proposed combined electrochemical and thermochemical water splitting cycle)[28].

$$S_8 + 8O_2 \text{ -> } 8SO_2,\ \Delta G^o = \text{-}300 \text{ kJ/mol } SO_2 \tag{1}$$

$$SO_2 + 2H_2O \text{ -> } H_2SO_4 + H_2,\ \Delta G^o = 85 \text{ kJ/mol; } E^o = 0.16 \text{ V} \tag{2}$$

In our SE model, sulfur is burned in air (equation 1) to produce SO_2. The SO_2 is then dissolved in a mixture of water and sulfuric acid and electrochemically converted into hydrogen and sulfuric acid (equation 2)[27]. A plant level box-diagram is shown in figure 1.

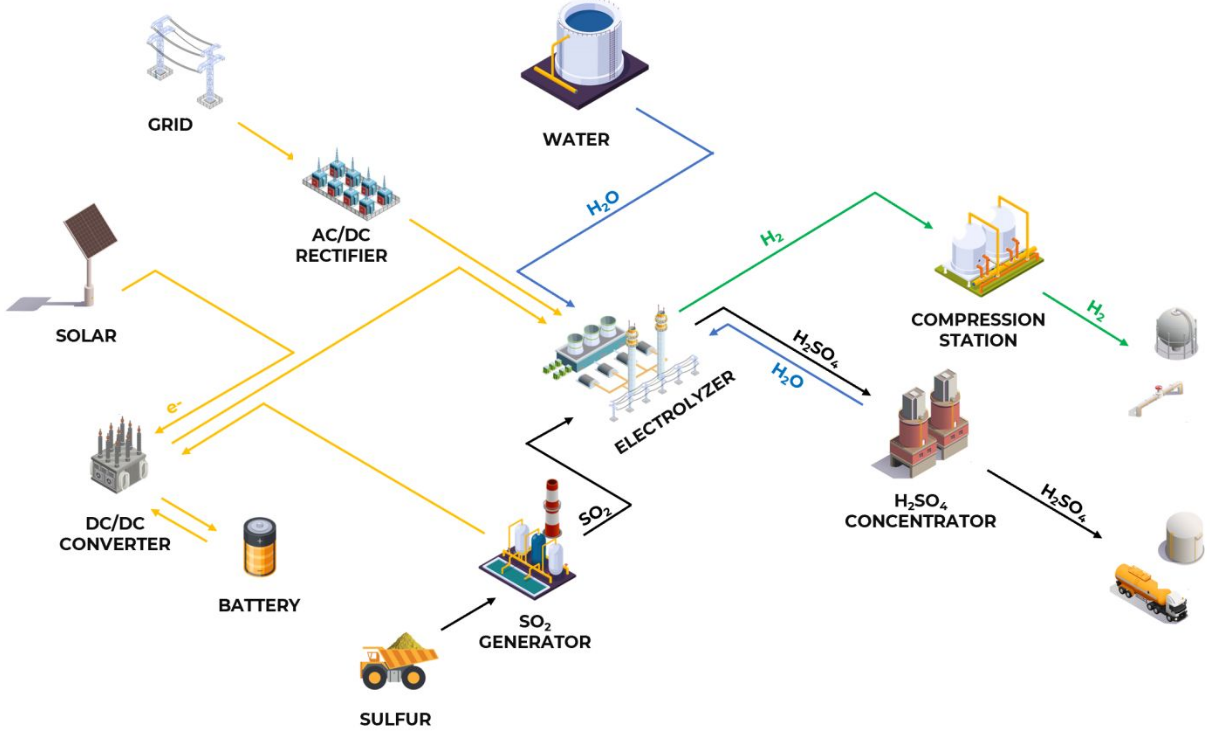


Figure 1: A simplified reactor scheme. Sulfur is burned in air and the resulting SO_2 is mixed with water where it is used in the electrolyzer as a raw material to cogenerate hydrogen and sulfuric acid. The sulfuric acid may be concentrated before use.

<u>Major Sulfur Electrolysis Plant Components</u>

SO_2 Generator: In the Contact Process, burning sulfur produces SO_2 and pressurized steam which is used to heat the downstream SO_3 generation reactor. Additional pressurized steam is produced when the SO_3 is hydrated to produce oleum and eventually sulfuric acid. The heat from this process is used to export as much as 0.2 kWhs electricity per kg of sulfuric acid for state of the art contact process plants[26]. In SE, the heat generated from burning sulfur (equation 2) is also turned into pressurized steam used to produce electricity for the electrochemistry. Our model assumes that 30% of the heat produced from sulfur burning could be used as electricity. In order to be consistent with a conservative estimate, we equated the CapEx of our sulfur furnace and turbine to the CapEx of an entire contact process plant which includes the CapEx required for electricity generation from burning sulfur (see Figure S1 and equation S1 for details)[27]. Under standard assumptions (see Table 1), as much as 12 kWhs/kg of H_2 were provided by burning sulfur.

Sulfur Depolarization Electrolyzer: Our techno economic analysis models a plant that utilizes industrial scale sulfur depolarization electrolyzers (SDEs). Because we are unaware of any industrial scale SDEs, we modified recent overnight CapEx numbers for Proton Exchange Membrane (PEM) water electrolyzers from the National Renewable Energy Laboratory's (NREL) H2A model[6]. Our model takes current OpEx and CapEx data and estimates the LCH. Some studies utilize a low-cost carbon-based electrolyzer (similar to a PEM fuel cell) as an electrolyzer with cell voltage of < 1 V. While the use of carbon instead of gold or tantalum coated titanium is an obvious way to reduce CapEx, our analysis did not consider this option[29]. The CapEx for electrolyzers in the H2A model assumes that each electrolyzer is capable of producing 500 kg H_2 per day and that the catalyst can reach a current density of 1.5 A/cm^2. It is likely that for a 500 kg H_2 per day electrolyzer that operates at a lower current density than in the H2A model, the electrolyzer would need to be bigger and therefore more expensive. To estimate the cost of an SDE ($CapEx_{lyzer\_SE}$) from a PEM electrolyzer, the PEM electrolyzer CapEx ($CapEx_{lyzer\_WE}$) was multiplied by the ratio of the operating geometric current densities of the water electrolysis catalyst (j_{WE}) to the SDE catalyst (j_{SE}) (see equation 3). It is difficult for most SDEs to reach current densities higher than 1.2 A/cm^2 without significant voltage losses due to mass transport limitations[17]. Equation 3 results in higher CapEx for SDEs than PEM electrolyzers, especially at high sulfuric acid concentrations where the dissolution of SO_2 is suppressed and the voltage increases due to concentration effects.

$$\mathrm{CapEx}_{\mathrm{lyzer\_SE}} = j_{\mathrm{WE}}/j_{\mathrm{SE}} \bullet \mathrm{CapEx}_{\mathrm{lyzer\_WE}} \quad (3)$$

Equation 3 also allows our model to tune the operating current density of the reaction because the relationship between voltage and current is non-linear such that energy consumption per kg H_2 decreases with decreasing voltage but the CapEx of the electrolyzer increases linearly with decreasing voltage. Our model uses this relationship to determine the cheapest operating current density for the plant. Figure S2 shows the calculated price of hydrogen for a variety of electrolyzer costs and operating current densities where the lowest price of hydrogen for a given CapEx and current density represents the optimized operating condition.

Sulfuric Acid Concentrator: Our model assumes that sulfuric acid and hydrogen were cogenerated in a SDE with currently demonstrated voltage, current, and faradaic efficiency relationships[28,30]. Most industrial applications use 62 to 98 mass percent (10 to 18 M) sulfuric acid. Studies have shown that modern SDE can generate 65% sulfuric acid and therefore, we assume that produced sulfuric acid must be concentrated for many applications (see key technical challenges below and Figure S3-S5, and equations S2-S6, and Tables S1-S2 for details)[28,30].

To account for acid concentration, we use real data from Sinopec Nanjing Chemical Industry Co. Ltd from a currently installed plant in Nanjing, China to add CapEx and OpEx values for sulfuric acid concentration via combined vacuum concentration and spent acid regeneration processes. Costs of raw materials, permitting, and labor are converted to US values to be consistent with the model.

General Model Considerations

Maintenance: As in the H2A model, we assume that maintenance requires replacement of 15% of installed CapEx every 7 years. Three percent of installed CapEx was added as annual OpEx to account for annual maintenance[2].

Energy Sources: There is a prevailing economic assumption that, with cheap enough solar electricity, any electrochemical process can make CO_2-free products for lower cost than grid electricity simply by running intermittently on solar energy[31]. We test this assumption by running the model in either grid-assisted with optional onsite solar mode or solar-only mode and comparing the results. In grid-assisted mode, grid electricity is used to supplement onsite solar with optional battery storage in the cheapest possible configuration. Solar-only mode only allows the model to use solar-derived electricity. Our model uses a value of $0.07 per kWh for grid electricity (the 2020 US industrial average)[23]. The cost of solar, similar to previous models, is calculated using three years of hourly resolved insolation data which was spatially averaged across the entire contiguous United States (CONUS; see supplemental materials for details)[32]. While there was considerable seasonal variation, the CONUS average solar capacity factor was 20%[32]. The solar panels in this analysis were assumed to have a peak power rating of 160 W/m^2 with a 0.75% loss in efficiency per year of operation. In grid assisted with optional onsite solar mode, solar panels were added beyond where their electricity was 100% directly used until the marginal Levelized Cost Of Energy (LCOE) for solar was higher than that of grid electricity. Optional batteries were rated to a constant annual discharge over a 12-year lifetime after which they would need to be replaced[33]. Costs associated with energy are presented in Table 3. All battery costs assume a 0.5 kW max power output/kWh energy storage[33]. The time of day or year that energy was needed could also be changed by increasing the number of electrolyzers and running them for less time per day or year (capacity factor). The capacity factor of the plant was allowed to vary between 1% and 97% of a year. The model optimized capacity factor, size of the onsite solar installation, energy drawn from the grid, and energy stored in batteries. Under standard assumptions, despite a 20% capacity factor for solar, 29% of energy needed was provided by solar while 71% was provided by the grid, no battery storage was used and solar panels were left open circuit when they were overproducing. Plant capacity factor was 97%. For the solar-only case, similar to analyses done on water electrolysis, due to high overall plant CapEx, it was cheaper to have a capacity factor of 97% and operate on battery based electricity than to decrease the capacity factor.

Table 2. CapEx and OpEx Associated with Energy.

Photovoltaics (PVs)[a]	
CapEx (USD/kW)	
Module	0.31
Hard Balance of Systems	0.22
Installation Cost	0.12
Soft Balance of Systems	-
OpEx (USD/kWyr)	17
LCOE[b] for First PV Panel (USD/kW)	0.043[c]
Batteries	
CapEx (USD/kW)	

Module	180
Hard Balance of Systems	60
Installation Cost	27
Soft Balance of Systems	33
OpEx (% installed CapEx/12 years)	69
LCOE [d] for First Battery (USD/kW)	0.21[c]

Note. [a]Similar to other studies, it is assumed that PV could be placed on top of all structures and therefore no soft balance of systems would be associated with PV[7]. [b]Levelized Cost of Energy. [c]This value agrees with previous studies[34].

Levelized Cost Calculation: Equation 4 calculates levelized costs; variable definitions follow: LC is the levelized cost (e.g. of hydrogen); product is the annual amount of product made (in kWhs for batteries or solar panels and in kgs for hydrogen or sulfuric acid); lifetime is the time the plant lasts before replacement in years; OpEx is annual operational expenditure; CapEx is the total capital expenditure of building a plant; r is the rate of return; and t is time in years. We assume a one-year build time where no product was produced. We also assume that plant capacity reached the maximum capacity factor during the first year of operation. We also assume a rate of return of 12% as standard. This is higher, and therefore more conservative, than the H2A model which assumes an 8% rate of return. Our model assumes no taxes, subsidies, or deferred debt.

$$LC = \frac{CapEx + \sum_{t=2}^{lifetime+1} \frac{OpEx}{(1+r)^t}}{\sum_{t=2}^{lifetime+1} \frac{Product}{(1+r)^t}} \tag{4}$$

Consistent with our conservative assumptions, when we use SMR CapEx and OpEx numbers from the H2A model, our model estimates an LCH of \$1.25 instead of \$1.15 per kg H_2. However, we use \$1.15/kg as our reference point for SMR which accounts for the relative riskiness of the new technology compared to the incumbent technology.

CO_2 Emissions Analysis: The amount of produced CO_2 varies for electrochemical processes based on how that electricity is generated (e.g. coal, natural gas, solar, biomass etc). Modern SMR emits around 9.28 kg CO_2 per kg hydrogen and is heated with natural gas[6]. This process is thermochemical with 59-83% of CO_2 being chemical process CO_2 emissions and the other 17-41% coming from heating[3]. The full process requires 41-46 kWhs per kg hydrogen of thermal energy and is net endergonic at the thermodynamic limit[35]. The net sulfur electrolysis process is exergonic; heat harvested from burning sulfur can be captured and converted into electricity to run the SDE. While it is theoretically possible to run the plant only on burning sulfur (without exogenous electricity) the assumed energy

consumption of the plant it too large for the assumed conversion efficiency of heat to electricity from the sulfur burner (30%) even at low operating voltages.

For emissions, we use an average emissions factor for US natural gas electricity of 0.41 kg CO_2/kWh because we assume that natural gas electricity is available wherever industrial hydrogen is needed (this emissions intensity is slightly lower than the US average of 0.44 kg CO_2/kWh)[36]. Electricity harvested from sulfur burning, PV, or PV plus batteries was assumed to emit no CO_2. If sulfuric acid concentrating was necessary, electricity and natural gas requirements were taken into account for the concentration step (see Tables S1,2 and Figs. S4,5 for details).

Sensitivity Analysis: We performed a sensitivity analyses to determine how the price of hydrogen would respond to several factors: electrolyzer current density, amount of produced hydrogen, CapEx of the components, catalyst stability, catalyst activity, process faradaic efficiency, catalyst cost, prices of sulfur and sulfuric acid, the rate of return, cost of electricity (from PV, grid, or batteries), and a CO_2 tax. For each sensitivity analysis, the parameter of interest was varied while the current density and capacity factor of the plant changed to find the cheapest possible plant configuration. All other parameters were set to constant values. Parameter values as well as ranges for values are presented in Table S1. Real data from lab scale SDEs were used for current density and corresponding voltages[28]. Current density was corrected based on an empirical relationship between voltage and faradaic efficiency (see Figs. S7-S9 and eqs. S4-S6 for details). A detailed discussion of the sensitivity parameter range selection may be found in Table S3

Comparing Cogeneration to SMR: It is difficult to make a direct comparison between SMR and cogenerative processes because SMR only makes a single hydrogen commodity while cogenerative processes make at least two commodities. For the purposes of this analysis, we make this comparison by subtracting out the revenue of selling the cogenerative commodity. In the case of SE, sulfuric acid may be sold at an US average of $100/tonne in 2018[37]. Another way of comparing these costs would be to subtract a levelized cost of sulfuric acid production via the contact process which would represent a maximum LCH ($6.83 per 49 kg H_2SO_4 according to our model). We find negligible differences between the methods. We present results from the former method because the selling price of sulfuric acid has been validated by the market whereas the levelized cost of sulfuric acid is an estimate (see tables S4 and S5 for details on levelized cost of sulfuric acid and hydrogen via the contact process and SMR).

Model Validation: We validated our model by comparing LCH values for both grid-assisted and solar-only WE hydrogen as well as the LCOE from solar. We found that all of these values agreed with previous studies as discussed in Table 3 and below[5,7,34]. We also considered, non-average conditions and found that our model was in good agreement with previous studies that showed the LCH from WE as low as \$2.93/kg with favorable geographic constraints and subsidies see Table S6 for details[21,22,24].

Results and Discussion

Levelized Cost of Hydrogen Under Standard Assumptions

Under standard assumptions, our techno-economic model estimates that the LCH from SE is \$0.51/kg H_2 when 96% concentration by mass sulfuric acid is cogenerated. This price is considerably lower than the LCH from SMR (Table 3). Next, we investigated the production of hydrogen using only solar-derived electricity. We found that the optimized solar-only LCH is \$2.32/kg H_2 when 96% concentration by mass sulfuric acid is cogenerated, more expensive than SMR (Table 3).

CO_2 Emissions Analysis

Under standard assumptions, the calculated cheapest price for hydrogen for SE was found when the reaction required 18 kWh/kg H_2 of exogenous electricity (30 kWh/kg H_2 if no electricity is harvested from sulfur combustion, see fig. S2). This happened to occur around the point where the current density switched from the mass transfer limited regime to the charge transfer limited regime (fig. S5). With an economically optimal solar penetration, SE was found to have fewer greenhouse gas emissions than SMR by almost a factor of two even if sulfuric acid needed to be concentrated to 96% (Table 3). Even though we are utilizing electricity from burning sulfur for SE, it may be fair to claim that if a state-of-the-art contact process plant were replaced with SE, 0.2 kWh of clean electricity may be lost for every kg of H_2SO_4 that is made. In which case, natural gas electricity may need to replace this demand, and the relative emissions intensity of SE would increase by 4 kg CO_2/kg H_2. This change would result in 9.03 kg CO_2/kg H_2 for 96% H_2SO_4, still lower than SMR (Table 3).

These data indicate that if SE were to meet the global demand for sulfuric acid (~3 Tmols in 2017)[25] and the produced hydrogen were to replace around 9% of global hydrogen demand as a commodity chemical, then up to 60 MMT of CO_2 emissions could be avoided by the use of grid assisted SE with onsite solar. Under a solar-only scenario, current technology for SE is not cheap enough to make hydrogen that is competitive with hydrogen from SMR. However, two ways to make clean SE cost competitive with SMR are to 1) levy a carbon tax of \$115/tonne of CO_2 for the solar-only version or 2) use a standard hydroelectric, nuclear, or geothermal grid at its current price[38]. Clean-energy-only SE could reduce CO_2 emissions by up to 145 MMT at full scale.

Future Sulfur Electrolysis Technology

Both H_2S and S_x have been investigated in electrochemical cells with coproduction of H_2 at the cathode (equations 5-7)[39–43].

$$xH_2S(g) \text{ -> } xH_2 + S_x(s),\ E^o = 33\ kJ/mol\ H_2;\ E^o = 0.14\ V \qquad (5)$$

$$S_x(s) + 2xH2O \text{ -> } xSO_2 + 2xH_2,\ \Delta G^o = 174\ kJ/mol\ H_2;\ E^o = 0.5\ V \qquad (6)$$

$$SO_2 + 2H2O \text{ -> } H2SO4 + H_2,\ 85\ kJ/mol\ H_2;\ E^o = 0.16\ V \qquad (7)$$

While equations 5-7 have been performed at the lab scale, we are not aware of long-term stability testing or other attempts to commercialize this technology. One major problem is deposition of solid sulfur on the cathode during oxidation of H_2S. To solve this problem, we used 50% sulfuric acid as an electrolyte and were able to maintain a cell temperature of 118°C which, at such high sulfuric acid concentrations, allowed liquid sulfur and liquid water to be present in the electrolyzer while preventing solid sulfur build-up. Despite the likelihood that this electrolyzer could be graphite-based due to the low operating voltages, we assumed that this future H_2S electrolyzer has the same CapEx as a present-day PEM electrolyzer which is more expensive than a graphite system[6,29]. Using a lab-measured JV curve for the rate limiting electrochemical oxidation of solid sulfur (Fig. S10) we can perform the same analysis as above. We assumed operation at < 1.23 V to ensure that water splitting is not contributing to faradaic losses.

Under this scenario, we find that hydrogen and 96% sulfuric acid could be produced at a 4:1 molar ratio for \$1.30 and \$0.97/kg H_2 using \$0.07 and \$0.06/kWh electricity prices respectively (Table 3). Unfortunately, with a natural gas grid assisting onsite solar, this process emits 9.8 kg CO_2 per kg H_2 and therefore is dirtier than SMR. However, with a 25% cleaner-than-natural-gas-grid (0.33 kg CO_2/kWh or less) this process would be cleaner than SMR. This grid could be achieved by using a mix of wind, hydro, nuclear, and geothermal which all have larger capacity factors than solar and may decrease the price of electricity[38]. This indicates that 4:1 molar ratio sulfur electrolysis could be a feasible pathway to produce up to ~36% (13 Tmol or 26 MMT) of the world's H_2 with some technological development. Importantly, it is feasible to make 1:1 and 4:1 clean SE that is cheaper than SMR using current technology prices for hydro and geothermal (LCOE \$0.05 and \$0.06/kWh respectively)[38].

Table 3: Summary of cost and emissions for various hydrogen production pathways. SMR is steam methane reforming, SE is sulfur electrolysis at a 1:1 molar ratio of H_2:H_2SO_4, SE4 is sulfur

electrolysis at a 4:1 molar ratio of H_2:H_2SO_4. All H_2SO_4 was concentrated to 96% by mass. These data are calculated under standard assumptions (Tables 1 and S3).

	Grid-Assisted Solar Energy		Only Solar Energy	
Production Process	**Cost ($/kg H_2)**	**Emissions (kg CO_2/kg H_2)**	**Cost ($/kg H_2)**	**Emissions (kg CO_2/kg H_2)**
SMR	**1.15**	**9.28**	**5.05**	**5.50**
SE	**0.51**	**5.03**	**2.32**	**0.00**
WE	**5.72**	**15.79**	**9.91**	**0.00**
SE4	**1.30**	**9.76**	**6.87**	**0.00**

Pathways to Cheaper, Clean Hydrogen

We conducted a sensitivity analysis to understand what would be necessary, aside from a carbon tax, for solar-only SE to outcompete SMR. We found that for SE, many individual improvements were more than enough to reduce the LCH to below that of SMR. These individual improvements include reducing the voltage requirement, reducing the solar or battery module CapEx, and reducing the balance of systems or electrolyzer CapEx (fig 2). Consistent with prior research on noble metal catalysts, even a 10X increase in the CapEx of the catalyst did not increase the LCH by more than 10%. These data indicate that with reasonable R&D improvements, solar-only SE may be cost competitive with SMR. A sensitivity analysis for grid assisted SE with onsite solar may be found in figs S10-S11.

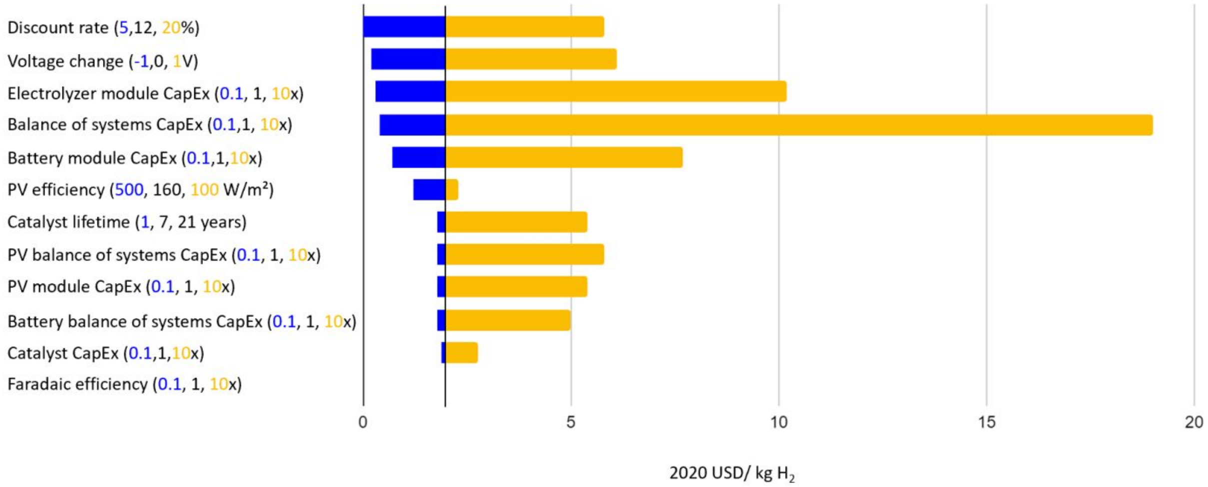


Figure 2: Sensitivity Analysis of Solar-Only Sulfur Electrolysis. The parenthetical numbers on the vertical axis indicate the low, standard, and high assumption for each case.

To simplify the sensitivity analysis, we analyzed the optimal system configuration for various total CapEx and electricity prices. In this analysis all component CapExes were reduced evenly. CapEx reductions made the model find new optimal operating currents, voltages, and capacity factors. Importantly, *we do not report $/kW for CapEx* because the optimum operating voltage and current (and therefore power) of a given system may change based on local prices of electricity and CapEx (fig. S2) which yields the metric inadequate for comparison especially across different chemistries. Figure 3 below shows the various combinations of energy price and CapEx that could allow grid-assisted-with-onsite-solar and solar-only sulfur electrolysis to outcompete SMR without a carbon tax.

A

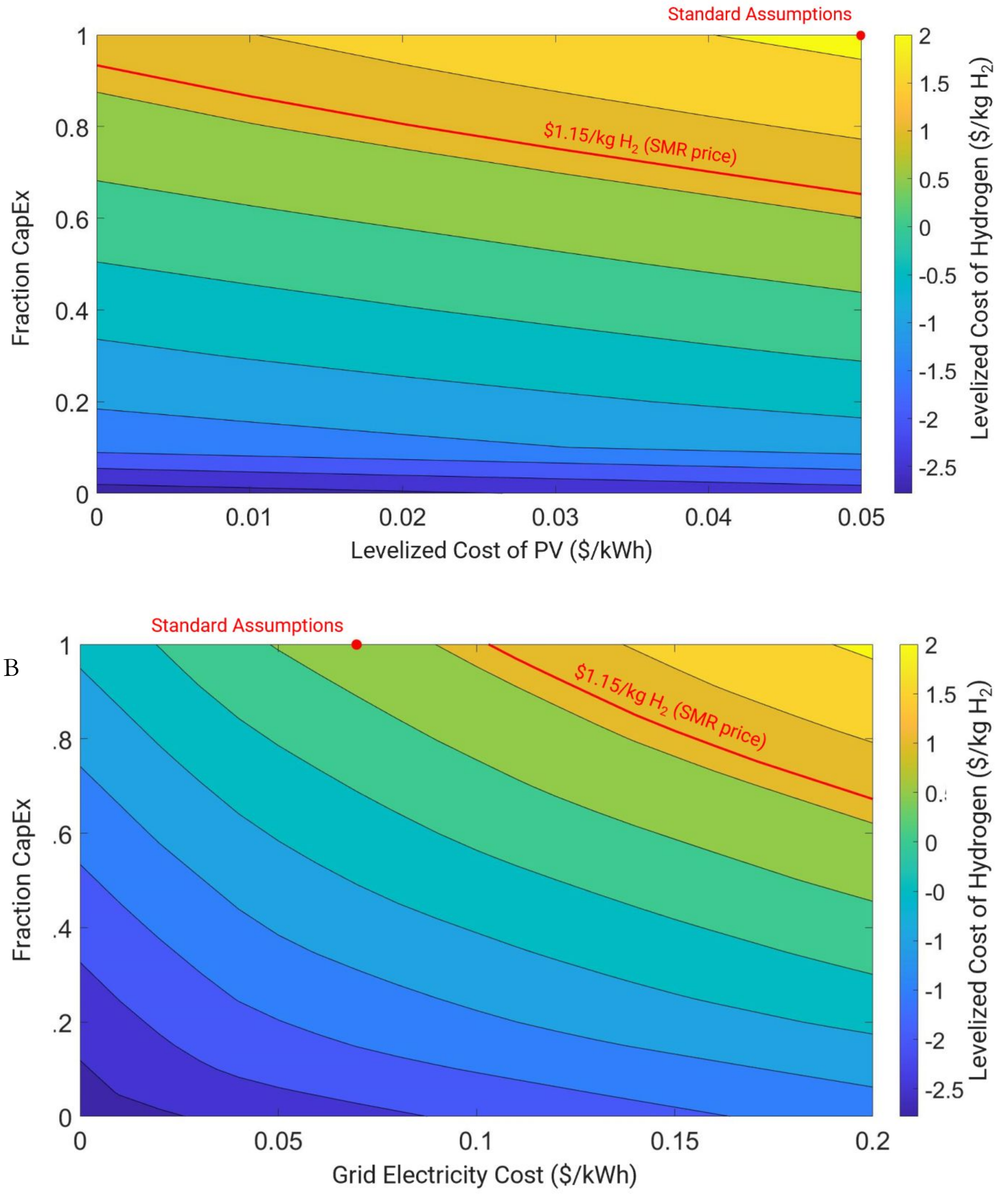


Figure 3: LCH of SE with various CapEx and Electricity Price Assumptions. 3A shows cost of solar-only SE while 3B shows SE with onsite solar assisted by a natural gas grid. All CapEx components were reduced evenly. For the grid assisted case, the solar LCOE was held at $0.043/kWh meaning that below that price, no solar was used.

Figure 3A shows that even with free PV electricity, CapEx must be reduced by ~10% to compete with SMR. CapEx reductions also reduce the price of grid-assisted SE with onsite solar. By comparing Figures 3A and 3B we can see that it is difficult for solar-only SE to be cheaper than grid assisted SE with onsite solar. In the scenario where grid-based electricity prices remain at \$0.07/kWh, solar-only SE could be cheaper than grid-assisted SE with onsite solar if solar electricity prices were \$0.05, \$0.02, and \$0.01/kWh if CapEx were to be 14X, 5.3X and 5X cheaper than current model assumptions respectively (Table 4). Another strategy to make 100% clean hydrogen that is cheaper than SMR could be to use present-day prices for hydro, geothermal, and some nuclear power or blended grids with >30% capacity factor (Table 4).

Comparison to Water Electrolysis

We then analyzed how the economics of making hydrogen from WE compare with SE including co-selling oxygen from WE (see figs. S8 and S9 for details on physical parameters of WE). We found that grid-assisted WE with onsite solar was \$5.72/kg H_2 and solar-only WE was \$9.91/kg H_2 (Table 3). These values are consistent with previous studies[5–7]. Solar-only WE would require a CO_2 tax of \$933/tonne to be cost competitive with SMR.

We conducted a sensitivity analyses on model parameters for solar-only WE, and we found that, unlike solar-only SE, no single improvement could reduce the LCH from solar-only WE to be competitive with SMR. Instead, at least three improvements needed to be combined to reduce the cost of WE to below \$1.15/kg H_2 (fig. 4). For example, if the peak power rating of PVs was increased from 160 W/m^2 to 500 W/m^2 (LCOE = \$0.014/kWh), and the CapEx of battery modules decreased by 10X (LCOE = \$0.025/kWh), along with at 10X CapEx decrease for electrolyzers and plant balance of systems, solar-only WE would be cheaper than SMR. Similar to previous findings, even reducing the CapEx of the catalyst by 10X would only reduce the LCH by 5%[7]. In all combinations of only three component CapEx reductions, the balance of systems CapEx must be reduced which is likely the hardest CapEx component to be reduced because it is made up of already mass-produced components. Therefore, it is likely that >3 system components must see ≥10X CapEx reduction for solar-only WE to be cheaper than SMR *and* grid-assisted WE with onsite solar.

Co-sale of oxygen is also a way to reduce cost for WE. Oxygen (the cogeneration product of WE) is an important industrial gas with an industrial demand of ~12 Tmols/year worldwide and a value of \$40/T[44]. This would mean that co-selling oxygen could result in an additional revenue of \$0.64/kg H_2 which would yield a cost of \$4.86 and \$9.21/kg H_2 under grid-assisted and solar-only assumptions respectively[44]. Therefore, co-sale of oxygen will not allow clean water electrolysis to be cost-competitive with current technology. These data indicate that many more improvements would need to be made to a WE system than to a SE system to make solar-only hydrogen production cost competitive with SMR.

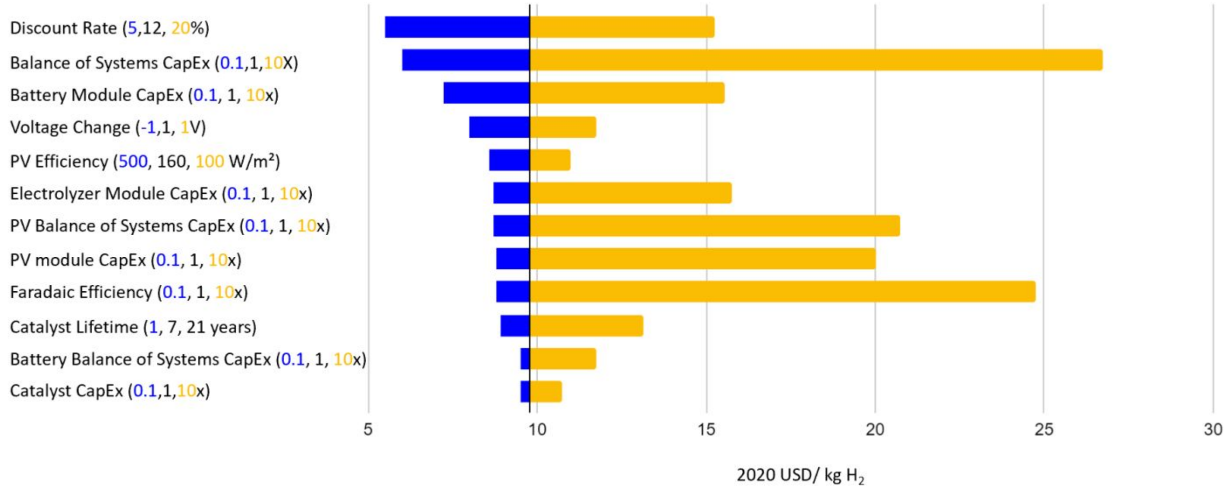
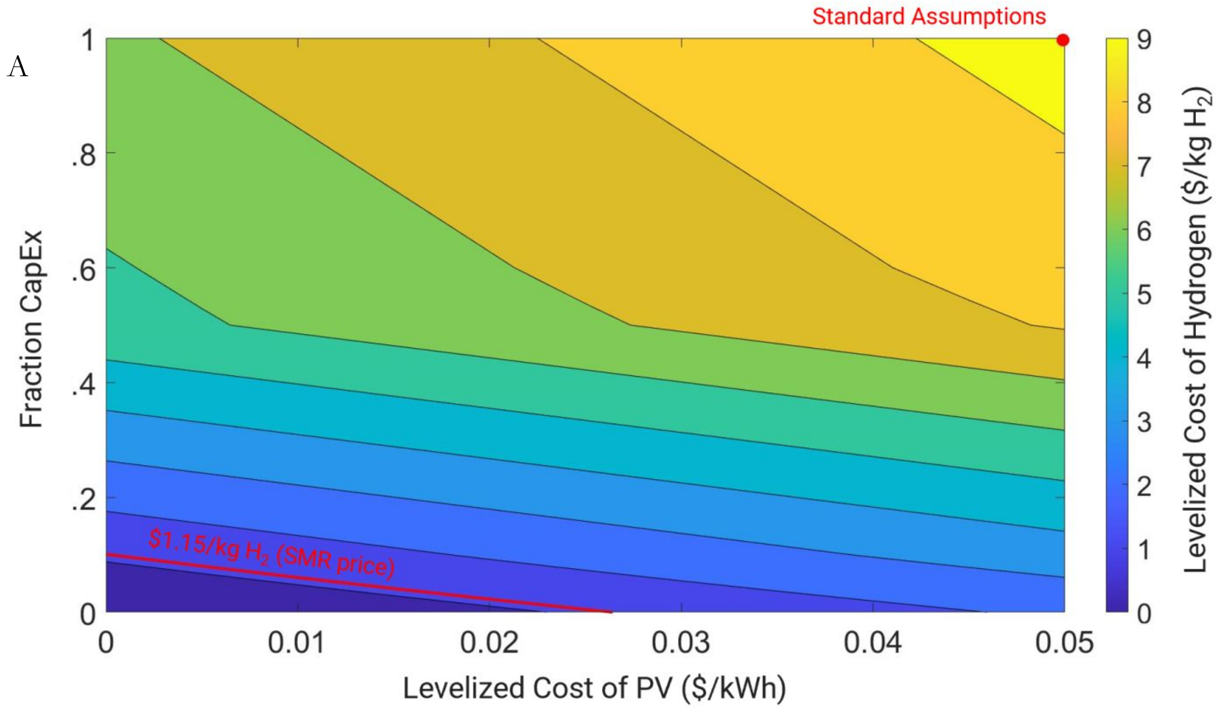


Figure 4: Sensitivity Analysis of Solar-Only Water Electrolysis. The parenthetical numbers on the vertical axis indicate the low, standard, and high assumption for each case.

Unlike SE which is cleaner than SMR even when onsite solar is assisted by a natural gas grid, grid-assisted WE with onsite solar is only cleaner than SMR when assisted by rare grids that are >65% cleaner than natural gas (0.18 kg CO_2/kWh) ignoring the contribution of solar to the grid (solar in the grid cannot be counted towards this number because it overlaps with the time that solar produces electricity onsite at the plant). In order for WE to be cheaper and cleaner than SMR, a >65% cleaner-than-natural-gas-without-solar-grid would need to be available 24 hrs/day and produce electricity that is <\$0.023/kWh. \$0.023/kWh is 2X cheaper than current hydroelectricity and solar electricity and 3X cheaper than the average US industrial electricity price. However, even at \$0.023/kWh this grid would still require CapEx to be free for WE to be cheaper than SMR (fig 5A). Importantly, unlike SE, there is no grid known to these authors that is both cheap enough *and* clean enough to allow WE to be cleaner and cheaper than SMR even with a 10X reduction in CapEx (requires \$0.015/kWh, 100% capacity factor, clean grid). However, a 10X reduction in CapEx could open the possibility of some extremely low-cost natural gas electricity (e.g. Alberta, Canada) to make WE cheaper than SMR but >1.5X more emissions intensive. If grid electricity remained at \$0.07/kWh and solar electricity fell to \$0.02/kWh (2X cheaper than today)[34] or \$0.01/kWh (4X cheaper than today)[34] and WE CapEx was

60X and 14X cheaper than it is today respectively, solar-only WE could be cheaper and cleaner than SMR and grid-assisted WE with onsite solar yielding a certainty of clean hydrogen (Table 4). Locations with highly abundant solar energy or other renewable energy would also allow for lower cost renewable-only installations than the standard assumptions in this model. To address this, we compared the price of SE and WE to SMR in five different renewable-only capacity factor scenarios including capacity factors which may only be obtained by blending multiple renewables and significantly upgrading grids to transport energy long distances to combat intermittency[45]. We calculated the cost of hydrogen for many average grids 20% (average USA solar)[32], 30%: (Saudi Arabia or California, USA Solar)[46], 50% (high capacity factor wind or blended wind and solar), 80%: (theoretical blended renewables)[32], and 100%: (theoretical all-renewables grid)[47]. We find that with standard CapEx, WE is more expensive than SMR and SE for all capacity factors at \$0.05, \$0.02, and \$0.01 per kWh and SE is cheaper than SMR for all electricity prices in 30%, 50%, 80%, and 100% capacity factors except \$0.05/kWh at 30% capacity factor (Table 4).



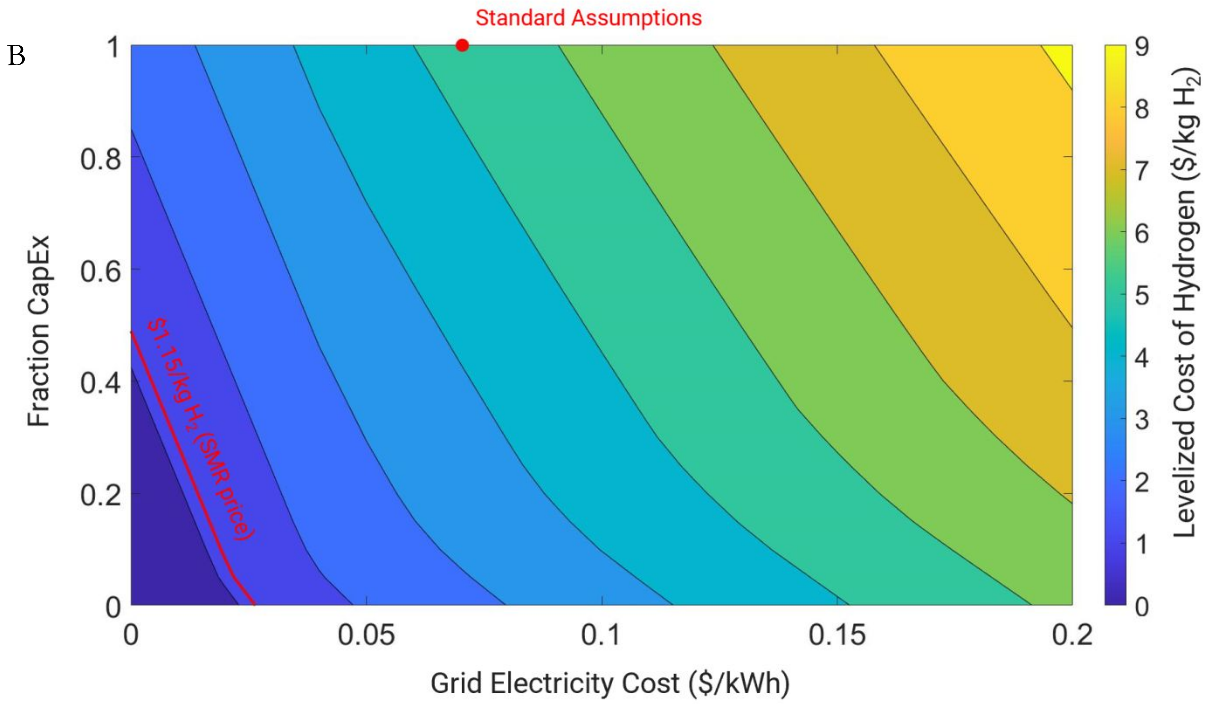


Figure 5: LCH of WE with various CapEx and Electricity Price Assumptions. 5A shows cost of solar-only WE while 5B shows WE with onsite solar assisted by a natural gas grid. All CapEx components were reduced evenly. For the grid assisted case, the solar LCOE was held at $0.043/kWh meaning that below that price, no solar was used.

Table 4: Required cost reduction factors of CapEx for solar-only electrolysis to be cheaper than SMR and natural-gas-grid-assisted electrolysis with onsite solar energy for various solar prices and solar energy capacity factors. This tables represents some of the economic conditions that would guarantee that electrolysis hydrogen is clean. Grid electricity was held at $0.07/kWh for this analysis.

Capacity Factor	LCOE Solar ($/kWh)	$0.05	$0.02	$0.01
20%	SE	14X	5X	5X
	WE	impossible	60X	14X
30%	SE	3X	0X	0X
	WE	impossible	35X	8X

50%	**SE**	**0X**	**0X**	**0X**
	WE	**impossible**	**27X**	**6X**
80%	**SE**	**0X**	**0X**	**0X**
	WE	**impossible**	**19X**	**4X**
100%	**SE**	**0X**	**0X**	**0X**
	WE	**impossible**	**15X**	**4X**

Conclusions

There is a prevailing notion that intermittent solar-based electricity can outcompete 24hr grid electricity to make clean, cheap hydrogen using WE. Because lower cost solar and CapEx also make 24hr operation cheaper, for intermittent operation to outcompete 24hr operation major cost reductions in CapEx must be achieved for both WE and SE (Table 4). Additionally, for solar-only WE to be cheaper than SMR, major reductions in the price of solar electricity must occur[34]. The relatively novel components of CapEx like electrolyzers and catalysts have a relatively large chance of being cheaper at scale because, unlike the balance of systems components, they are not already mass produced. These novel components are sufficiently impactful on price to make solar-only SE, but not solar-only WE the cheapest option even if these components were free (figs. 2, 4). In order to make WE solar-only, CapEx reductions would need to occur in components that are already mass produced and typically have traveled very far down their cost curve since their invention, in some cases over 100 years ago. These CapEx components primarily include balance of plant costs like cement, steel, piping, wiring, voltage converters, and pumps. Additionally, while the cost of solar electricity is still decreasing, the trend is flattening, and, with the current trend, it may take more than a decade before the unsubsidized price of solar is cheap enough to make it possible for WE to be cheaper than SMR[34]. Therefore, we believe that the chances of solar-only WE competing with SMR and grid-assisted WE with onsite solar is relatively remote and significant attention should be paid to other hydrogen generation technologies like SE which appears to be more economically feasible in the near term.

In our opinion, a more likely scenario for WE and SE is that relatively modest CapEx reductions (0X-10X) will occur which rely on major cost reductions in relatively novel components (e.g. electrolyzers and batteries) paired with a reduction in solar prices to \$0.01-0.02/kWh. This will allow grid assisted or battery supported SE with onsite solar, but not WE, to make hydrogen that is cheaper than SMR when run at a near 100% capacity factor solar-based energy supply (figs 2-5).

In 2020, average CONUS industrial grid electricity prices vary from \$0.16/kWh in California to \$0.05/kWh in Oklahoma with an average of \$0.07/kWh, the number used in the study. The US

Energy Information Agency (EIA) estimates the LCOE for behind-the-meter (i.e. onsite at the plant) generation for hydroelectric, geothermal, and combined cycle natural gas can be even cheaper at \$0.05, \$0.04, and \$0.04/kWh respectively. Of these technologies, combined cycle natural gas is the only one that is not geographically constrained. Advanced nuclear is also not geographically constrained and is CO_2-free, however, it is estimated to be around \$0.08/kWh. Supercritical coal is \$0.07/kWh. According to figures 3B and 5B all of these technologies are currently cheap enough to make hydrogen via SE competitive with SMR but none are cheap enough to make WE hydrogen competitive with SMR. Furthermore, using any of the energy sources to make hydrogen with SE, except coal which is more expensive, would lead to a decrease in CO_2 emissions. Unfortunately, using any fossil electricity source to make hydrogen with WE would lead to an increase in emissions. This suggests that SE but not WE may be a near term solution to producing abundant, clean hydrogen. We acknowledge that SE alone cannot produce the world's hydrogen, so below we define criteria to identify candidate reactions to produce the world's demand for hydrogen cogeneration while reducing cost and CO_2 emissions.

Opportunities for Co-production to make the world's hydrogen demand clean.

Below are a criteria for identifying novel hydrogen cogeneration chemistries that may be both cleaner and cheaper than SMR in the near term.

1) There should be an annual demand of at least 0.1 Tmol for the co-product. Small industrial plants produce ~0.1 Tmols (0.2 MMT) H_2/year[4] so we chose a 0.1 Tmol/year global demand minimum for the co-product. Some chemicals that surpass this threshold are lime (for cement, ~47.5 Tmols/year)[48], oxygen (~12 Tmols/year)[44], ammonia (~10.5 Tmol/year)[49], methanol (~4.5 Tmols/year)[50], sulfuric acid (~3.25 Tmol/year)[25], propylene (~3 Tmols/year)[51], formaldehyde (~2.5 Tmols/year)[52], ethylene (~1 Tmol/year)[53], benzene (~1 Tmol/year)[54], carbon black (~1.2 Tmols/year)[13], chlorine (~0.75 Tmols/year)[15], caustic soda (~0.75 Tmols/year)[15], and nitric acid (0.1 Tmols/year)[55]. With these products combined, even at a 1:1 molar ratio, there is more than enough cogeneration capacity to produce the world's current hydrogen demand[9].

2) At least one of the co-products must be oxidized from a readily available starting material. Hydrogen is a fully reduced product and therefore requires the oxidation of something else to produce it. Some of the products, like ammonia, are very difficult to co-produce with hydrogen, because they are also fully reduced and would need to be produced in a scheme that cogenerates both ammonia and hydrogen with at least one additional oxidized byproduct. Other potential coproducts could be produced oxidatively depending on the starting material. Benzene, for example, could be co-produced with hydrogen if synthesized solely from methane or other alkanes, but not solely from more oxidized reactants like alkynes. There may also be multiple ways to produce a given product to enhance hydrogen production. For example, propylene synthesis produces one mol hydrogen per mol propylene, however, in theory, propylene could also be synthesized from three mols of methane which would create three mols hydrogen per mol propylene. Finally, products like lime may not be produced as a sole co-product because there is no readily available source of reduced calcium metal. However, lime may be produced, for example, from limestone in a combined reaction scheme with water splitting that also produces CO_2[56].

3) The thermodynamic minimum cost and emissions of the product should be at least parity with the market standard. Because 24 hr operation is typically cheaper than intermittent operation with current, and likely future, technology, a good candidate that shows the potential to make low emissions, low cost hydrogen is: 1: lower emissions than SMR when using natural gas electricity or heat after the industry standard emissions for the co-product is subtracted (eq. 3) and 2: is lower cost than the conventional production when the co-product value is subtracted (eq. 4). If the actual energetics, OpEx, and CapEx of the process is not known, an easy way to screen processes is to use the minimum amount of energy (approximated as ΔG^o) along with the relevant price of energy while assuming that all other OpEx and all CapEx is zero.

$$U * e_c + N - Q \lesssim U_{SMR} * e_{SMR} + N_{SMR} + U_P * e_P$$

(8)

&

$$U * d_c + O_c + C_c - P \lesssim U_{SMR} * s + O_{SMR} + C_{SMR}$$

(9)

U is energy, e is emissions intensity for the type of energy in a given location, and N is process CO_2 emissions ($N_{SMR} = 5.5$ kg CO_2/kg H_2), Q is the emissions associated with the normal way of making the co-product, d is the cost of the energy, O is the OpEx of the system assuming the energy type, C is the CapEx of the system assuming the energy type (CapEx will change based on capacity factor of the energy type and other variables), and P is the co-product value. Subscripts c, b, p and SMR mean cleaner energy type, base case energy type, conventional production pathway of the co-product(s), and steam methane reforming, respectively.

Using the criteria above, figure 6 shows that at least 57 Tmol/year of hydrogen (160% of the world's demand for industrial hydrogen) may be cogenerated with another commodity chemical in an overall reaction scheme that yields hydrogen and may be cleaner and cheaper than hydrogen produced via SMR with 2020 US energy assumptions. Chemical reactions that do not meet the above criteria include electrochemical production of nitric acid and WE (but not thermochemical water splitting). Because the price of heat is cheap compared to electricity, and electricity is so easily turned into heat, thermochemical processes to make these chemicals may prove to be lower cost and emissions than electrochemical processes and may also be easily converted into electric processes when electricity becomes cheap enough via resistive heating. Furthermore, many of the chemicals in figure 6 are already produced where hydrogen is used at refineries (benzene, chlorine, and propylene) or fertilizer plants (sulfuric acid) and therefore would make logical cogeneration targets. Water splitting, however, is only cleaner than SMR if heat is used and therefore, WE does not pass the minimum bar in this analysis to be considered as a clean hydrogen production pathway. Given the urgency of the climate problem, we urge significant research efforts be devoted to these cogenerative pathways to realize near-term CO_2 emissions reduction targets.

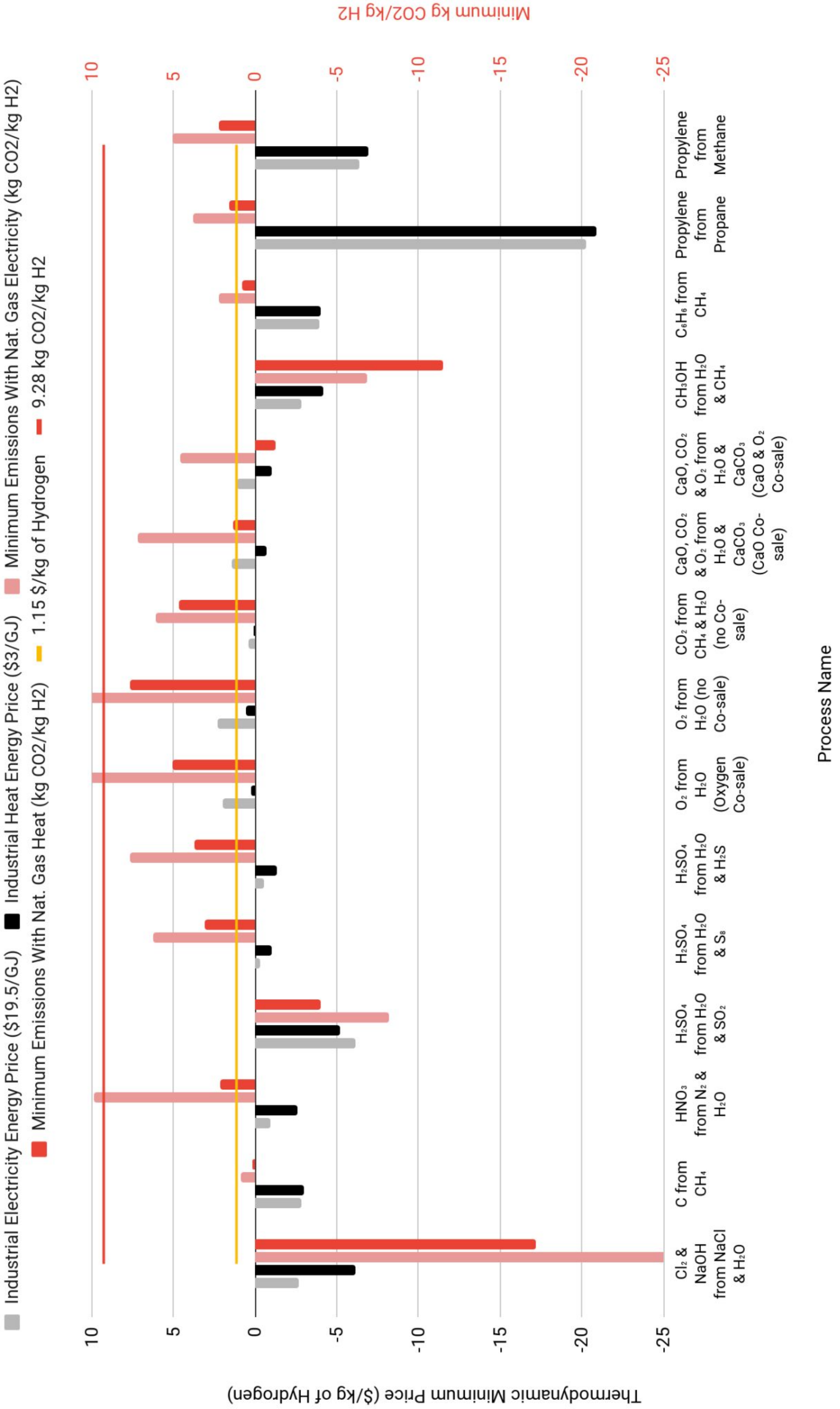

Industrial Electricity Energy Price ($19.5/GJ)
Industrial Heat Energy Price ($3/GJ)
Minimum Emissions With Nat. Gas Electricity (kg CO2/kg H2)
Minimum Emissions With Nat. Gas Heat (kg CO2/kg H2)
1.15 $/kg of Hydrogen
9.28 kg CO2/kg H2
Thermodynamic Minimum Price ($/kg of Hydrogen)
Minimum kg CO2/kg H2
10
5
0
-5
-10
-15
-20
-25
Process Name
Cl₂ & NaOH from NaCl & H₂O
C from CH₄
HNO₃ from N₂ & H₂O
H₂SO₄ from H₂O & SO₂
H₂SO₄ from H₂O & S₈
H₂SO₄ from H₂O & H₂S
O₂ from H₂O (Oxygen Co-sale)
O₂ from H₂O (no Co-sale)
CO₂ from CH₄ & H₂O (no Co-sale)
CaO, CO₂ & O₂ from H₂O & CaCO₃ (CaO Co-sale)
CaO, CO₂ & O₂ from H₂O & CaCO₃ (CaO & O₂ Co-sale)
CH₃OH from H₂O & CH₄
C₆H₆ from CH₄
Propylene from Propane
Propylene from Methane

Figure 6. Minimum costs and emissions of various hydrogen cogeneration pathways. These costs are calculated using \$3/GJ (\$0.01/kWh) heat, \$0.07/kWh (\$19.5/GJ) electricity, no CapEx, no non-energy OpEx, and using ΔG^o as the energy demand. Emissions were calculated using natural gas as the energy source. The value of the co-product was subtracted from the cost of the energy. Baseline energy and CO_2 emissions were calculated for each coproduct based on the endnoted references: chlorine and caustic soda[16], carbon black[57], nitric acid[58], sulfuric acid[27], lime[59], oxygen[60], methanol[61], benzene[62], propylene[63].

Because the climate problem is urgent, hydrogen production is responsible for ~3% of global CO_2 emissions, and the above analysis suggests that making technologies that are cheapest when run intermittently will require considerable technological advances, we urge the community to research technologies, like SE, which can make hydrogen for lower cost and lower emissions than SMR on currently available energy resources like hydro, geothermal, and natural gas. We also encourage more research into technologies which could produce continuously available, low cost, clean energy like advanced nuclear or ultra-low cost solar plus pumped hydro or compressed air storage. A clean, low cost, continuous grid, may pave the way for cogeneration of hydrogen with commodity chemicals and possibly environmentally benign byproducts like oxygen or potentially carbon.

Conflicts of interest

H.F.L, D.Z., M.R.H., and N.A.F.'s institution (California Institute of Technology) has filed a U.S. patent application directly relating to the work described in the paper (patent application no. US20190376191A1, filed on May. 17, 2019). C.E.F., H.L., and E.T.K. are founders or employees of Brimstone Energy Inc., a company which has hydrogen co-generation its vision.

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