

Solar fuel processing: Comparative mini-review on research, technology development, and scaling

Sophia Haussener

Laboratory of Renewable Energy Science and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

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ABSTRACT

Solar energy provides an unprecedented potential as a renewable and sustainable energy resource and will substantially reshape our future energy economy. It is not only useful in producing electricity but also (high-temperature) heat and fuel, both required for non-electrifiable energy services. Fuels are particularly valuable as they are energy dense and storable, and they can also act as a feedstock for the chemical industry. Technical pathways for the processing of solar fuels include thermal pathways (e.g. solar thermochemistry), photo pathways (e.g. photoelectrochemistry), and combinations thereof. A review of theoretical limits indicates that all technical solar fuel processing pathways have the potential for competitive solar-to-fuel efficiencies (>10 %) but require very different operating conditions (e.g. temperature levels or oxygen partial pressures), making them complementary and highly versatile for process integration. Progress in photoelectrochemical devices and solar thermochemical reactors over the last 50 + years are summarized, showing encouraging trends in terms of performance, technological viability, and scaling.

1. Introduction

The global primary energy consumption is significant (606 EJ in 2019) and dominated by non-renewable resources (86 % based on oil, coal, natural gas, and nuclear) (Key World Energy Statistics, 2021). The growth rate has varied and slightly decelerated in recent years but is still as high as 7.19 EJ/y (average rate over the last 30 years). The environmental, economic, health and societal challenges related with the emissions associated to the life cycle (incl. mining, processing, utilization etc.) of these resources is one of the grand challenges of modern time. A large variety of scenarios have been investigated, indicating that four strategies can be followed to induce and accelerate a transition from a fossil fuel-based energy economy towards a sustainable one: i) decarbonization of energy services (electricity, heat, fuel), ii) increase of energy conversion efficiency, iii) increase of renewable energy utilization, and iv) electrification of energy services (World Energy Outlook; Williams et al., 2012; World Energy Scenarios, 2019; Jacobson et al., 2017). Decarbonized electrification is a very important parameter in this transition. However, even with very ambitious electrifications targets, there remains a significant amount of energy services that will be difficult or not meaningful to electrify. Fuels for long-range and freight transportation in the mobility sector, on-demand high-temperature heat for industry, seasonal storage for year-round residential energy services,

and feedstock and commodities for chemical process industry will partially rely on such non-electrical services, requiring still annually ~ 200–300 EJ as heat and fuel. Ideally, this energy should be provided sustainably and flexibly in scale, i.e. small-scale and decentralized (such as e.g. in single units, remote houses) all the way to large-scale and centralized (such as in a fuel processing plant). When reviewing the five renewable energy resources, it is apparent that solar energy has the largest (theoretical) potential to fill this gap (Lewis, 2007). Less than 1 % of the earth surface receives our annual global energy demand. Additionally, solar energy can be variably converted into all energy carriers and vector of interest, including electricity, low-temperature heat, high-temperature heat, fuels (such as hydrogen) and chemical commodities (such as hydrogen, CO or syngas). Solar collectors for low-temperature heat for residential and industrial applications are commercialized and so is solar electricity by photovoltaics or concentrated solar. Solar collectors for residential and industrial applications of 480 GW, concentrated solar power plants of 5.5 GW, and photovoltaics of 512 GW have been installed by 2018 (Secretariat). Photovoltaic electricity has even emerged as one of the most cost competitive sustainable electricity choices (Newman et al., 2012). Technologically more challenging are the utilization and storage of solar energy for high-temperature heat applications or for solar fuels and chemical commodities (hydrogen, hydrocarbons, ammonia, etc.) (Lewis, 2016; Trainham et al., 2012). The

E-mail address: sophia.haussener@epfl.ch.

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largest barriers for the technical implementation of these solar solutions on the large-scale are related to maturity and cost of the technologies. Here, I will review and compare the possible solar fuel processing pathways, with a particular focus on solar hydrogen, CO and syngas.

2. Solar fuels: Nature versus technical alternatives

A competitive technical solution for the production of a solar fuel such as hydrogen, needs to show excellent performance (high efficiency, excellent selectivity, large production rates, high conversion etc.), operate for long lifetimes (reduced degradation, stable and robust operation, etc.), be versatile in product and fuel type produced, be economically competitive (price per kg of hydrogen, investment and operating cost, etc.), be sustainable (large energy return on investment, low greenhouse gas emissions, low ecotoxicity, etc.), and be scalable (Ardo, 2018). Natural photosynthesis is the obvious competition to technical solar fuel processing solutions. Natural photosynthesis has annually-averaged solar-to-biomass efficiencies below 1 %, with few exceptions that show efficiencies of up to 3 % (e.g. microalgae) (Blankenship et al., 2011). In terms of efficiency, it seems possible to beat nature. A first challenge appears in the longevity and lifetime. Nature has the ability to self-repair and operate without interventions for tens to hundreds of years while technical solutions require significant maintenance and replacements to achieve similar lifetimes. In terms of versatility, nature provides all kinds of different types of biomass, including a variety of complex hydrocarbons. And finally, nature is already scaled, where a large fraction of the earth surface is covered with plants, i.e. photosynthetic units.

3. Technical solar fuel generation approaches and theoretical limits

The technical solutions for solar hydrogen (excluding bio-hybrids) include *i*) solar thermochemistry (direct water dissociation or thermochemical redox cycles), *ii*) photovoltaics coupled with high-temperature electrochemistry, *iii*) high-temperature photovoltaics (e.g. based on thermionic emission) coupled to high-temperature electrochemistry, *iv*) photovoltaics coupled with room-temperature electrochemistry, *v*) photo-thermal catalysis, *vi*) photoelectrochemistry, and *vii*) photocatalysis. Fig. 1 shows a graphic representation of the pathways, with

decreasing temperatures from the left to the right side (for the non-hybrid pathways in the center). There is a possibility for hybridization for the thermochemical (Nzihou et al., 2012; Piatkowski et al., 2010; Steinfeld, 2005) and photo(electro)catalytic (Uekert et al., 2018; Uekert et al., 2021) approaches. That is, there is a pathway for solar-only operation with low-value reactants (e.g. water, CO₂, N₂) but also for a hybrid solar/fossil (or solar/biomass) operation, where the carbonaceous feedstock originates from fossil fuels (or waste products such as various forms of plastics) or biomass while the reaction enthalpy (for endothermic reactions such as water splitting) comes from the solar input. These hybrid approaches can also be seen as decarbonization processes (Romero and Steinfeld, 2012).

Typically, photon-driven pathways are limited in the utilization of the solar irradiation given by the bandgap of the materials. Recently, approaches to thermally integrate photoelectrochemical devices have been proposed, indicating a possible pathways to partially recover some of the low energy photons and thermalized energy (Tembhurne et al., 2019). On the other hand, thermally-driven approaches typically rely on relatively large temperatures that cannot easily be achieved without solar-tracking concentrating facilities. Concentrating facilities reduce the utilization of the solar radiation to the direct part of the solar light. The absorption behavior of the receiver and reactor surfaces is typically high and relatively constant over the spectrum, also a result of receiver and reactor designs that resemble black bodies (Steinfeld and Schubnell, 1993) (i.e. with apparent emissivity close to 1). Comparing the direct fraction of the solar radiation (i.e. direct normal irradiance - DNI) with the radiation that is received by a non-tracking solution (i.e. global horizontal irradiance - GHI), they both can be similar, however highly dependent on location and its latitude. This highlights that there is no inherent performance advantage between a sun-tracking concentrating technology and a non-tracking non-concentrating technology (if locations are optimized appropriately). Ideas for a better utilization of the solar spectrum lead to photo/thermal combinations and approaches depicted in the center of Fig. 1, including solar-driven high temperature electrolysis, photo-thermal approaches, thermally integrated photoelectrochemical approaches (Tembhurne et al., 2019), or further coupling of approaches for co-generation schemes (e.g. fuels and electricity) (Wang et al., 2022).

Calculations and predictions of theoretical and limiting solar-to-hydrogen efficiency have been conducted for all different processes

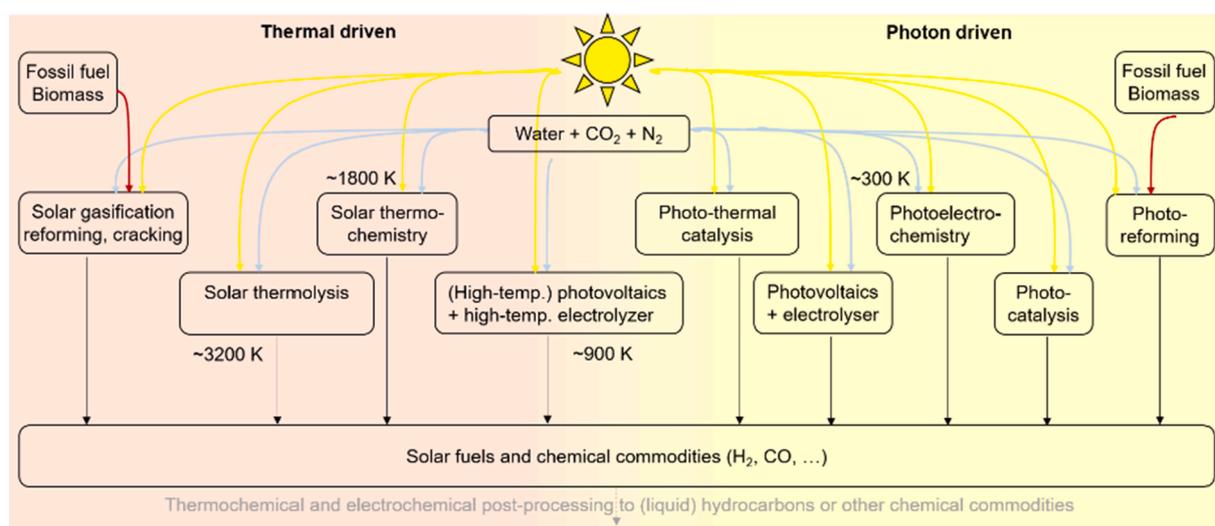


Fig. 1. Schematic representation of the various technical solar fuel and chemical commodities pathways (with a particular focus on hydrogen). Left side highlights thermally-driven pathways such as solar thermolysis or solar-thermochemical cycles, right side highlights photon-driven pathways such as photocatalysis or photoelectrochemistry. The center represents pathways that make use of the thermal as well as photon energy. The left/right border pathways highlight possible hybrid approaches that combine solar-driven chemistry with carbonaceous feedstock. The products (hydrogen, CO, ...) can further be processed to dedicated chemical commodities in subsequent chemical reactions.

(on device and/or system scale) and a select number is compiled and compared in Fig. 2 (focusing on hydrogen). These calculations have to be compared with care, given the different system boundaries, assumptions, and consideration of real or hypothetically optimized materials. However, this summary provides a general idea of ranges of achievable efficiencies and required operating temperatures.

Solar thermolysis requires temperatures in excess of 3000 K and, while experimentally demonstrated (Kogan, 1998), has significant technical challenges (e.g. requires semipermeable high-temperature stable membranes). It is not further discussed here. A way to reduce the operating temperature and separate the oxygen evolution from the hydrogen evolution process is through solar thermochemical multi-step redox cycles (Steinfeld, 2005). These redox cycles have been investigated with various redox materials (Haeussler et al., 2018; McDaniel, 2017; Scheffe and Steinfeld, 2014; Abanades et al., 2006), where the two-step cycle with ceria has evolved as a reference. Thermodynamic analyses of solar hydrogen processing cycles with ceria have been conducted based on sweep gas (with the addition of oxygen scavengers) and vacuum pumping approaches incorporating different temperature and pressure swings (Bader et al., 2013; Ermanoski et al., 2014; Lapp et al., 2012; Lin and Haussener, 2015), resulting in peak solar-to-hydrogen efficiencies in the range of 12–20 %, at reduction temperatures significantly above 1500 K. These systems require elevated gas-to-gas heat exchange options (here assumed heat exchanger effectiveness of 96 %) and a tight control of the oxygen partial pressure during the reduction step in order to reach these efficiencies. Assumptions and implementations with respect to reactor flow and equilibrium conditions (Li et al., 2018; Bulfin, 2019; Brendelberger et al., 2015) can affect the estimated efficiency values but do not significantly change the ranges shown here. Approaches for solid-to-solid heat recovery, (Lapp et al., 2013; Felinks et al., 2014) transition towards isothermal operation with pressure swings (Muhich et al., 2013; Warren et al., 2022), or alternative redox materials (discovered and guided by high-throughput testing and characterization (Park et al., 2021) and artificial intelligence) (Bayon et al., 2022; Li, 2022) could help to further improve the performance.

Reduction in operating temperature is possible if part of the thermal input to the process is replaced by electrical energy. High-temperature electrolysis driven by solar electricity (either photovoltaic (PV) or concentrated solar power (CSP)) represents such an option. Techno-economic analysis of such a system indicated that solar-to-hydrogen efficiencies in the range of 7–17 % can be achieved at temperatures in the range of 1000–1400 K, dependent on the heat integration scheme (Lin and Haussener, 2017). The requirements for the oxygen partial pressure are significantly less severe, i.e. allowing 1 atm of air at the anode. However, thermally-induced mechanical failure are a concern, given that high-temperature electrolyzers are typically made of relatively brittle ceramic components. Theoretical studies on the reactor-scale of the integrated solar-driven high-temperature electrolysis reactor indicate that a combination of the solar receiver and high-temperature electrolysis into one single reactor might further increase the performance and reduce the losses (Lin et al., 2022; Lin and Haussener, 2018). Such approaches are predicted to reach efficiencies of ~ 20 % at slightly reduced temperatures of 1000 K. However, the losses due to system auxiliary devices are not yet considered.

On the opposite side of the temperature range, i.e. at low temperatures, are the near room-temperature operating photocatalytic (PC) and photoelectrochemical (PEC) pathways. Calculations, considering hypothetical and optimized photoabsorber materials, predict solar-to-hydrogen efficiencies in the range of 19–31 % (Tembhurne et al., 2019; Fountaine et al., 2016) for PEC (single versus dual junctions) and 16–31 % for PC (single versus dual absorber configurations) (Nandy et al., 2021). For PEC, an increase in the theoretical efficiencies has been predicted if thermal integration between the photoabsorber and electrocatalysts is considered (Tembhurne et al., 2019). All these calculations consider catalytic and transport losses. The consideration of auxiliary components in a complete system (pumps, separators,

compressors, etc.) would further reduce the expected performance. The identification of materials that fit the theoretically predicted best candidates and that are stable is ongoing and relies also on high-throughput synthesis and characterization, supported by artificial intelligence tools (Green, 2017; Yan, 2017; Stein and Gregoire, 2019). While thermo-mechanical stability is not a main concern in PEC and PC devices, they suffer significantly from degradation due to the direct semiconductor-electrolyte interfaces, and typically approaches to increase longevity include the introduction of protection layers or the separation of the semiconductor from the electrolyte (Walter et al., 2010). Longevity remains one of the main technical challenges of PEC devices (Ager et al., 2015). For comparison, the efficiency of a current, mature solar hydrogen system composed of PV plus low-temperature electrolysis components (silicon PV with 20 % efficiency, and polymer electrolyte membrane electrolysis with 70 % efficiency, resulting system efficiency of 14 %, without auxiliary components) is also indicated.

A relatively novel concept of high-temperature photovoltaic devices (for example based on the thermionic emission principle) and its combination with high-temperature electrolysis has been proposed (Gutierrez and Haussener, 2021; Ye et al., 2013; Kribus and Segev, 2016). This approach tries to push the limit on thermal integration for PEC and aims at a solid-state PEC device alternative. Operation at these higher temperatures (above 500 K) hold the promise of being able to utilize more abundant materials (for example as catalysts) and to reduce the equilibrium and (reaction and transport) overpotentials. Initial calculations predict 10–12 % solar-to-hydrogen efficiencies on the device-level at temperatures in the range of 600–700 K (Gutierrez and Haussener, 2021).

Overall, it appears that solar energy conversion approaches span a wide range of temperature and a similar range of solar-to-hydrogen efficiencies. A comparative theoretical loss analysis between photoelectrochemical and solar thermochemical approaches is described Cheng et al. (Cheng et al., 2021) and a comparison for the various solar fuel approaches with respect to cost and sustainability is described by Song et al. (Song et al., 2022) General considerations of material availability and their criticality should also be considered when comparing the various approaches (Vesborg and Jaramillo, 2012). For all approaches, competitive (>10 %) efficiencies will be achievable in well-designed systems, no matter whether room or high-temperature and thermal or photo-driven solar hydrogen/fuel processes are pursued. The temperature range between 300 and 500 K might provide novel opportunities for solar fuel processing and potentially profit from progress in fields such as reduced-temperature proton conducting membranes.

All calculations represent theoretical potentials and limits, some with more accuracy and consideration of realistic effects and losses than others (i.e. device versus system-level, ideal versus real materials, etc.). Below, a mini review of actual demonstrations and the corresponding performance metrics (efficiencies, production rates, selectivities, conversion, and longevity) is given.

4. Demonstrations and state of the art

An overview over the various solar hydrogen generation demonstrations is given in Fig. 3. Note that efficiency definitions for solar thermochemical approaches are typically based on the high heating value of hydrogen (or CO or syngas), while efficiencies for photocatalytic or photoelectrochemical approaches are typically based on the Gibbs energy of hydrogen (or CO). Only device demonstrations with complete overall water or CO₂ splitting reactions are considered, with a focus on hydrogen, CO, and syngas products. Examples of the correspondingly implemented reactor concepts are shown in Fig. 4.

The first demonstration of the photoelectrochemical effect (Fujishima and Honda, 1972) did not resemble an independently operational device and was conceptually simple, relying solely on a photocatalyst, counter electrode and electrolyte. The stringent material requirements

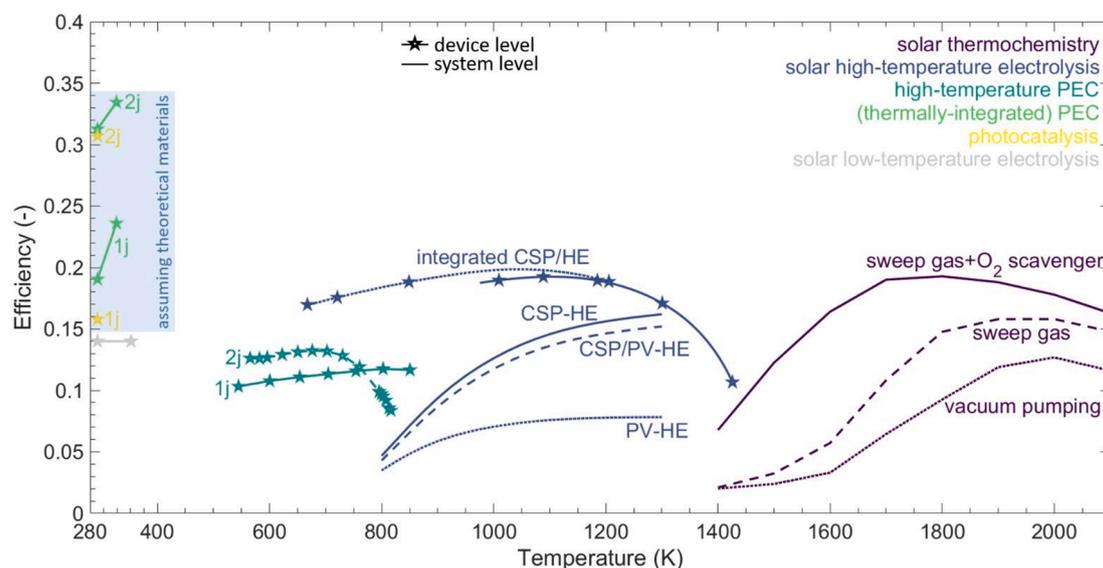


Fig. 2. Solar-to-hydrogen efficiency as a function of temperature for various solar-driven processing routes: Solar thermochemical systems using ceria (violet) and operating with sweep gas and gas-phase heat recovery (and oxygen scavenger) and vacuum pumping options (Lin and Haussener, 2015), solar-driven high-temperature electrolysis systems (blue) with thermal (CSP-HE), electrical (PV-HE) and thermal-electrical hybrid (CSP/PV-HE) options (Lin and Haussener, 2017), solar-driven integrated high-temperature electrolysis device (blue) (Lin et al., 2022), high-temperature photoelectrochemical systems and devices (turquoise) with single and dual junction options (Gutierrez and Haussener, 2021), thermally integrated and non-integrated photoelectrochemical devices (Tembhurne et al., 2019; Fountaine et al., 2016) (green) with single and dual junction options (indicated as 1j or 2j, respectively) of theoretical materials, photocatalytic devices (Nandy et al., 2021) (yellow) both with single and dual junction options of theoretical materials, and commercial PV plus low-temperature electrolysis device (grey). PC and PEC routes consider reaction and transport overpotentials. Analyses on the device level are indicated with star markers, analyses on the system level (i.e. including auxiliary components) have no markers. Temperature for the thermochemical approaches represents the reduction temperature, for the solar high-temperature electrolysis approaches the electrolysis temperature, for the integrated high-temperature electrolysis approach the average between cavity and electrolysis temperature, and for all other photo-electrochemical approaches the average of the photoabsorber and electrolysis temperatures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

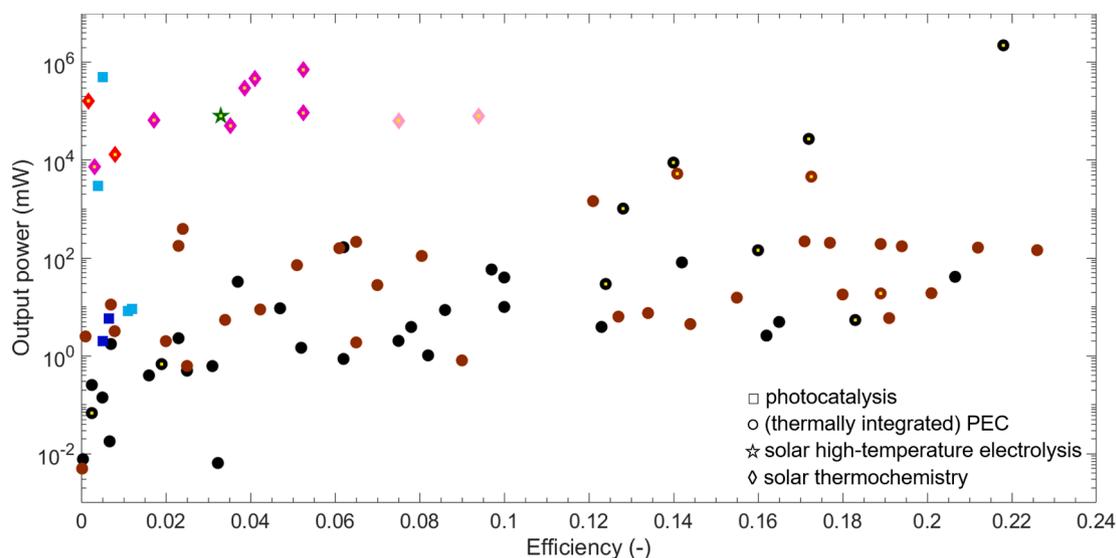


Fig. 3. Comparison of experimental demonstrations in terms of solar-to-fuel efficiency and output power. Blue squares represent demonstrations with photocatalysis particles (dark blue in suspension (Takata et al., 2020; Qi et al., 2018), light blue as catalyst sheets (Wang, 2017; Wang, 2016; Goto et al., 2018) including a multi-panel large-scale demonstration (Nishiyama et al., 2021) for hydrogen. Black dots show (thermally integrated) PEC demonstrations for hydrogen based on summaries in (Tembhurne et al., 2019; Ager et al., 2015); (See also dynamic comparison tool <http://specdc.epfl.ch/> and online database <https://solarfuelsdb.epfl.ch/>) and large-scale demonstration on EPFL campus (Holmes-Gentle et al., 2022), brown dots for CO based on summary in (Boutin, 2022) (efficiency only considers CO and neglects co-production of hydrogen). The green pentagram is a demonstration of an integrated CSP/HE reactor for hydrogen (Lin et al., 2022). Red diamonds represent solar thermochemical hydrogen demonstrations integrated over reduction and oxidation steps (Chueh et al., 2010; Koepf et al., 2016), pink diamonds are based on syngas or CO production demonstrations (Hathaway et al., 2016; Furler et al., 2012; Marxer et al., 2017; Furler et al., 2012; Koepf, 2019; Schäppi et al., 2022; Zoller et al., 2022) (efficiency of the large-scale demonstration (Koepf, 2019) is assumed 5.25%), both considering the sweep gas penalty in the efficiency definition. Light pink diamond represent two demonstrations excluding pumping and inert gas energy penalties (Haeussler et al., 2018; Abanades and Haeussler, 2021). Yellow center dots indicate demonstrations with concentrated irradiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

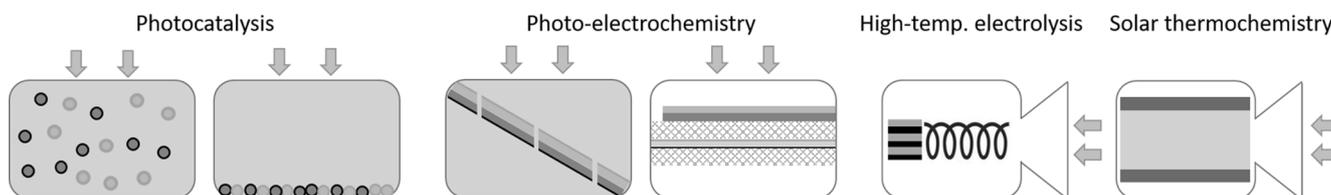


Fig. 4. Schematics of select reactor concepts for photocatalytic (suspension and catalyst sheet), photo-electrochemical (immersed photoelectrode and integrated PV plus electrolysis), integrated solar-driven high-temperature electrolysis, and solar thermochemical solar fuel and commodity processing approaches.

(Walter et al., 2010) later proved to be non-surmountable and instead a functional decoupling into multiple materials and components (absorber, co-catalysts, protection layers, etc.) has been pursued, leading to more than 40 successful complete device demonstrations (Tembhurne et al., 2019; Ager et al., 2015),¹. The largest solar-to-hydrogen efficiency demonstration is just below 21 % (Chang et al., 2017) (not considering demonstrations with more than one electrolyzer unit, although this design scheme allows for efficiencies as high as 31 % (Jia, 2016)). A first attempt of scaling was already reported in 1975 through a module of 20 photocathodes (Fujishima et al., 1975). Scaling can involve three strategies: *i*) increasing of the photoabsorber area, *ii*) the connection of multiple units into a larger module, and *iii*) the utilization of concentrated irradiation. The largest scale demonstrations (based on output power) are all operating with concentrated irradiation (up to 500 suns, i.e. 500 kW/m² (Peharz et al., 2007)) and are up to 30 W (Tembhurne et al., 2019). An on-sun demonstration of 2.21 kW output power at 21.8 % reactor efficiency is reported at EPFL (Holmes-Gentle et al., 2022). Lifetime of PEC devices is limited to hours or days (Ager et al., 2015), mostly resulting from significant degradation at the electrode–electrolyte interface (Nandjou and Haussener, 2017). PEC has also been explored for CO₂ reduction, where product selectivity is a major challenge. Relatively large selectivity towards CO (in the range of 90 %) has been achieved with silver catalysts, while other products, such as methane, ethylene or propylene, are possible with copper catalysts but typically with lower selectivity. The majority of solar-driven PEC CO₂ reduction demonstrations are targeting CO as product, with demonstrated solar-to-CO efficiencies (neglecting the co-production of hydrogen in the efficiency calculation) of up to 20 %. Effectively, these demonstrations produce syngas with H₂/CO ratios between ~ 0.1 and ~ 9. The conversion of CO₂ is often significantly lower than 10 %, even below 1 %. Dependent on the desired product and electrolyte configuration, the conversion is theoretically limited to below 50 % or even 25 % (Huang et al., 2021), highlighting reactant conversion as a challenge. More recently also for photoelectrochemical CO₂ reduction concentrated radiation (up to 450 suns) has been applied (Boutin, 2022).

Demonstrations of photocatalytic suspensions have exhibited solar-to-hydrogen efficiencies below 0.65 % (Takata et al., 2020) and are typically in the 2–6 mW output power scale (Nandy et al., 2021; Fabian, 2015). These efficiencies have been pushed to 1.2 % if the photocatalytic particles are immobilized onto substrates (called photocatalytic sheets) (Wang, 2017). For such sheets, large-scale demonstrations with multiple panels (total 100 m² area) resulting in a 500 W output power demonstration plant have been built and operated for multiple months (Nishiyama et al., 2021). Extension of photocatalysis and photocatalyst sheets to CO₂ reduction have been explored but with similarly low efficiencies. Irradiation concentration has not yet been considered for photocatalytic suspension reactors and photocatalyst sheet installations.

Solar thermochemical demonstrations involve a variety of different reactor concepts (Koeppf et al., 2017). They include a rotating cavity design (Koeppf et al., 2016; Schunk et al., 2008) and a gravity-fed film design (Koeppf et al., 2012) (both applied to ZnO/Zn), a receiver with

honeycomb structure design applied to mixed iron oxides (Agrafiotis, 2005), a multi-tubular particle flow concept investigated for hercynite (Martinek et al., 2014), a rotating ring design investigated for ferrites (Diver et al., 2008) and ceria (Lapp et al., 2013), a concentric multi-tubular design with integrated heat exchange investigated for ceria (Hathaway et al., 2016), a moving particle bed concept investigated for ceria (Ermanoski et al., 2013), and a receiver reactor with a porous ceria cylinder (Chueh et al., 2010; Furler et al., 2012). Not all of these concepts have ultimately been realized. The requirement of low oxygen partial pressures during the reduction step implies an energy penalty for the use and recycling of the inert sweep gas. This penalty is considered in all but two of the efficiency reports depicted in Fig. 3. Early on in solar thermochemistry, water as well as CO₂ splitting was considered, and currently mostly syngas or CO is the targeted product. The H₂/CO ratio can be tailored based on the water vapor and CO₂ feed, and with typical ratios that can vary between 0.25 and 2.34 (Furler et al., 2012). The highest achieved solar-to-hydrogen/CO efficiency reported is 5.25 % in temperature-swing operation and a reactor with porous cylinder of ceria (Marxer et al., 2017). This type of reactor was used in the on-sun demonstration of the complete sun plus air to kerosene processing chain, with a peak reactor efficiency of 3.86 % (Schäppi et al., 2022) and scaled to a solar tower system (Zoller et al., 2022). The same porous ceria reactor concept was also operated in vertical position, with a reported peak efficiency of 7.5 % and 9.4 %, however these efficiencies do not account for the energy penalties due to the sweep gas and pumping (Haeussler et al., 2018; Abanades and Haeussler, 2021). A concentric multi-tubular reactor with porous ceria and operated in isothermal mode achieved 1.72 % (Hathaway et al., 2016). Successful large-scale demonstrations with input power in the range of ~ 50 to 100 kW have been reported. One utilized a rotating cavity design for the ZnO/Zn cycle with an output power of 162 W, a result of the low efficiency (0.17 %) that was particularly affected by the low Zn yield (Koeppf et al., 2016). Two other demonstrations used porous ceria reactors, with an estimated output power of ~ 700 W (and estimated 5.25 % solar-to-CO efficiency) (Koeppf, 2019) and 462 W (Zoller et al., 2022). Conversion of the reactant, particularly CO₂, in the range of 80 % have been achieved (Marxer et al., 2017). Long term cycling tests with up to thousands of cycles have been reported for ceria and suggest that the mechanical and chemical stability is of limited concern (Chueh et al., 2010; Venstrom et al., 2014; Furler et al., 2014; Gladen and Davidson, 2016).

One single demonstration of an integrated CSP/HE reactor is reported and shows 3.3 % solar-to-hydrogen efficiency at an output power of 80 W (Lin et al., 2022), with significant potential for improvement lying in optimizing the solar received design and improving thermo-mechanical stability of the high-temperature electrolyzer.

It is observed (Fig. 3) that demonstrations based on a photo-electrochemical approach typically reach higher efficiencies than demonstrations based on photocatalytic or solar thermochemical approaches. Solar thermochemical and photocatalytic sheet demonstrations have reached output powers surpassing 100 W. There is one demonstration for a thermally-integrated PEC at EPFL that is surpassing the 1 kW output power scale. The majority of these larger scale demonstrations (with the exemption of photocatalytic sheet demonstrations) utilize highly concentrated irradiation (above 100 or even 1000 concentrations).

¹ See also dynamic comparison tool <http://specdc.epfl.ch/> and online database <https://solarfuelsdb.epfl.ch/>

The integration of photocatalytic, photo-electrochemical, solar-driven high-temperature electrochemical, or solar thermochemical processes with subsequent, typically continuously (24 h) operated thermal or chemical processes might require the addition of storage options. For this purpose, thermal processes can store upstream of the reactor the (high-temperature) heat and photon-driven processes potentially the separated charge carriers (i.e. electricity). For all solar fuel processes, the hydrogen (or feedstock) can be stored downstream of the solar reactor before being delivered to a subsequent processing step.

5. Conclusions

More than fifty years of solar fuels and artificial photosynthesis research have brought considerable advancements and achievements. Starting with the demonstration of the effect and approach (e.g. photoelectrochemical water splitting or solar thermochemical two-step water splitting), we have now achieved device and reactor demonstrations with competitive efficiencies (5–15 % solar-to-fuel efficiencies) at considerable scale (100 s W output power scale even above 1 kW), some of which have been developed into full technologies ready for commercialization. Solar thermochemical syngas processing has been combined with Fischer-Tropsch for solar liquid fuel production (i.e. kerosene) (Marxer et al., 2015) and more recently even utilizing water and CO₂ input from the air to provide a truly circular and sustainable solution for liquid fuels (Schäppi et al., 2022). Solar thermochemical CO production could be combined with photoelectrochemical hydrogen production to simultaneously profit from high selectivity and high efficiency. Solar thermochemical (Bader et al., 2017) as well as photoelectrochemical (Jin, 2018) principles have shown to be extendable to other chemical reactions (e.g. ammonia production) and can be combined with other processes (e.g. solar redox flow battery), making them interesting for a large variety of applications and for integration into a large variety of processes. Specifically, they can become versatile cogeneration systems and inter-sectoral technologies, solutions that will shape the future sustainable energy economy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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