Solar reforming as an emerging technology for circular chemical industries

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Abstract

The adverse environmental impacts of greenhouse emissions and persistent waste accumulation are driving the demand for sustainable approaches to clean energy production and waste recycling. Solar reforming is an emerging technology that is now transitioning from fundamental research towards practical application. By coupling the thermodynamically favourable oxidation of waste-derived organic carbon streams with fuel-forming reduction reactions suitable for producing clean hydrogen or converting CO_2 to fuels, solar reforming simultaneously valorises waste and generates useful chemical products. With appropriate light harvesting, catalyst design, device configurations and waste pre-treatment strategies, a range of sustainable fuels and value-added chemicals can already be selectively produced from diverse waste feedstocks, including biomass and plastics, demonstrating the potential of solar-powered upcycling plants. This review highlights the chemistry and compatibility of waste pre-treatment, introduces process classifications, explores the mechanisms of different solar reforming technologies, and suggests appropriate concepts, metrics and pathways for various deployment scenarios in a net zero carbon future.

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[H1] Introduction

The global environmental crisis encompasses a wide range of anthropogenic effects on the natural environment. This includes extreme weather patterns, rising sea-levels, irreversible loss of biodiversity and increased risk of diseases due to a greenhouse gas (GHG)-driven increase in global average temperatures[1,2], as well as pollution of soil, air and water by industrial and consumer waste[3]. GHG emissions are primarily driven by the excessive use of fossil fuels to meet the rising energy demand[4,5], causing the global atmospheric CO_2 concentration to rise continuously and reach record heights each year (423 ppm in 2023 compared to a pre-industrial average of 280 ppm)[6]. At the same time, consumers discard in excess of 2 billion tons of municipal solid waste (MSW) every year which contributes to 5% of GHG emissions[7]. Unmitigated, temperatures will continue to rise and waste will continue to accumulate, creating irreversible environmental damage.

In addressing global warming, the Glasgow Climate Pact 2021 established at COP26 recognised the urgency of the problem and reaffirmed the global goal to limit the Earth's temperature rise to 1.5 ºC above pre-industrial levels to alleviate the risks associated with climate change[8,9]. However, achieving this target is a mammoth task and can only be attained through technological innovations, combined with stringent planning and implementation from key stakeholders. Hydrogen, for instance is considered a frontrunning clean energy vector to replace fossil-fuels[10], but its current production relies primarily on CO_2-emitting steam reforming of methane. Such 'grey' hydrogen accounts for >95% of global production, releasing 830 Mt-CO_2 per year (~2.3% of annual emissions)[10]. Industrialisation of CO_2-neutral hydrogen production methods is critical for hydrogen to be considered a realistic 'green' alternative energy vector[10]. There is an urgent need not only for an accelerated effort in phasing out polluting, fossil-fuel based technologies, but also for the rapid development and deployment of efficient, sustainable, emission-free and cost-effective storable energy systems and processes[9].

Another concerning issue is the growth in annual MSW disposal, which is expected to rise from ~2 billion tonnes at present to 3.4 billion tonnes by 2050 with increasing per capita income levels[7]. Among the different types of MSW, biomass derived from food and plant matter (lignocellulosic biomass) constitutes more than 60% of the total volume globally[7]. Plastics account for a relatively small fraction (~12%) of the total waste generation[7], but pose an outsized threat to marine and terrestrial ecosystems owing to their non-biodegradability[11]. Weathering of large plastic objects breaks them down into micro- and nanoplastics that can enter the food-chain and may cause toxicity[12]. These processes happen so quickly that it was recently revealed that microplastics can already be found in human blood[13]. With low recycling rates (average of 4% and30% for low and high income countries, respectively), the disposal strategy for the majority of MSW (global average ~70%) involves open dumps and landfills, which contribute 1.5–2 billion tonnes, or 4% - 5.5%, of annual CO_2 emissions[7]. If no effective mitigation strategies are adopted, CO_2-equivalent yearly emissions related to solid-waste disposal are expected to reach 2.6 billion tonnes by 2050[7].

The chemicals sector is emblematic of our current, predominantly linear economy (Fig. 1). It continues to be driven by fossil fuels, accounting for 30% of total industrial energy use and 14% of global oil demand, with half used as chemical feedstock and the other half for energy production to power chemical processes[14]. The change towards a net zero chemicals sector constitutes a major long term challenge and requires the complete phasing-out of fossil fuels as materials input, with all carbon and hydrogen feedstocks being replaced by atmospheric CO_2, green hydrogen and recycled chemicals products or waste[14]. The need to transition to a sustainable economy is already driving the transition within several economic sectors; a recent report predicts the tipping point (that is, the transition from niche to mass market) of the chemicals industry to occur as the last industry sector only in 2030-35, approximately 15 years after green electricity generation[15]. This ongoing shift and time-line also carries important implications for entrepreneurs and innovators: it is an excellent timing to deliver and explore the commercial potential for breakthrough technologies in the next few years. This transformation needs to proceed at a feasible rate with affordable economics, creating opportunities to rapidly scale disruptive technologies.

One possible approach in addressing the issues of MSW disposal and GHG emission simultaneously is the utilisation of these abundant carbon waste resources as feedstocks for the generation of clean fuels and industrially relevant, value-added chemicals (Fig. 1). Existing waste-to-fuel or waste-to-chemical technologies are scarce and rely on energy-intensive strategies such as pyrolysis and gasification, which require high temperatures and pressures, and are typically carbon-positive[16]. Therefore, efficient and non-polluting technologies operating under ambient conditions are needed to create a sustainable circular network for waste valorisation, clean fuel generation and the consequent mitigation of GHG emissions,

Solar reforming is an emerging technology that uses sunlight to convert waste streams into fuels and chemicals (Fig. 1). This method has the potential to work directly on solid waste substrates but often requires pre-treatment as a critical step to solubilise the waste's polymeric components (for example, plastics and biomass). Here, we present a comparison of existing sunlight-driven technologies for waste reforming, with emphasis on catalyst development, deployment architecture, production rates and value creation. This review complements existing reports on the fundamental chemistry behind pre-treatment[17] and solar reforming processes[18] by outlining how this knowledge can be combined with state-of-the-art devices to enable circularity in the chemistry economy. The range of chemical processes that can be applied for catalytic conversion of biomass and plastic is vast and their economical deployment is a critical factor in sustainable solar reforming, providing a wide scope for exploration to identify environmentally benign and economically viable processes[17]. We will therefore touch briefly on waste pre-treatment and other supporting topics such as scalable catalyst design. The intent for this review to introduce readers to the state-of-the art in solar reforming and propose future directions and insights towards the development of practical solar-powered chemical industries for reforming diverse waste streams to fuels and chemicals, leading to value creation.

[H2] Definition and classification of solar reforming

Solar reforming is the sunlight-driven transformation of waste substrates into valuable chemical products. It provides some advantages over typical reforming (using processes like gasification) such as operation at ambient temperature and pressure. Solar reforming also introduces a thermodynamic advantage over the primary method for green hydrogen production, water splitting ($H_2O \rightarrow H_2 + \frac{1}{2}O_2$, $\Delta G° = 237$ kJ mol^{-1}), by coupling a reduction half reaction ($2H^+ \rightarrow H_2$ or $CO_2 \rightarrow$ products) with the oxidation of organic waste compounds ($C_xH_yO_z + (2x-z)H_2O \rightarrow (2x-z+y/2)H_2 + xCO_2$; $\Delta G° \sim 0$ kJ mol^{-1}). Archetypical photon-driven reforming reactions have utilised classical semiconductor photocatalysts, such as TiO_2, that rely on ultraviolet (UV) or near-UV irradiation and termed 'photoreforming'. Here, we define solar reforming to encompass processes that use energy from the wider solar spectrum, including UV and visible light (solar catalytic reforming) or can exploit the infrared (IR) region (solar thermal reforming) for waste valorisation purposes to create products of high economic value (that is, overall value creation must be greater than substrate value destruction). Thus, the use of expensive sacrificial electron donors to enable solar-driven processes to generate low-cost fuels does not classify as solar reforming. Solar catalytic reforming can be further categorised into three deployment architectures: photocatalytic (PC) reforming, photoelectrochemical (PEC) reforming, and photovoltaic-electrochemical (PV-EC) reforming (Fig. 2).

[H1] Waste streams and pre-treatment approaches

Most waste resources are polymeric and their intermolecular interactions, such as hydrogen bonding or crosslinking, make them insoluble under aqueous conditions and recalcitrant towards chemical transformations[16,17]. They therefore often require a pre-treatment step before they can be used in a solar reforming process to depolymerise the substrate into monomers able to participate in chemical reactions (Fig. 3). The nature of the depolymerised substrates, which come from the raw waste streams after pre-treatment, also plays a critical role in solar reforming performance[16]. Scaling sustainable solar reforming benefits from the use of water as the solvent. Therefore it is paramount for pre-treated substrates to be soluble in aqueous conditions, which favours substrates with high polarity and polarisability[19]. Moreover, the pre-treated substrates must have functional groups that can be readily oxidised (such as –OH, –CHO and α-H)[16,19]. In addition, the size, complexity and oxidation potential of the substrates also need to be considered. Sterically bulky substrates may have low aqueous solubility and result in poor interaction with the oxidation catalyst[20]. Finally, to keep the overall process economic and sustainable, mild and cost-effective pre-treatment strategies are preferable to energy-intensive or strongly corrosive approaches[16].

[H2] Biomass

The majority of the world's waste accessible for recycling and upcycling is biomass, primarily from agriculture and forestry sector residues, with an annual production of ~4 Gt yr^{-1} (around 3% of the global annual production of biomass, including natural detritus, which exceeds 140 Gt yr^{-1})[21]. In addition, ~66% of MSW is comprised of food, garden, paper and cardboard wastes, adding another 1 Gt of accessible biomass waste[7]. Most of this biomass, including inedible biomass from agricultural and forestry sources or some forms of food waste (for example cereals, fruit and vegetable peels), is lignocellulosic (or starchy) in nature and composed of three crosslinked and interconnected polymers[22]: cellulose (~40–50%) and hemicellulose (~25–30%) are polysaccharide carbohydrates useful for reforming processes and make up the majority of this biomass, with lignin (~15–20%), a non-carbohydrate structural polymer, and proteins making up the balance[23]. Lignin is a robust, highly-complex polyphenolic macromolecule that provides strength and hydrophobicity to plant cell walls and protects the polysaccharides from microbial degradation. It is a key factor for recalcitrance of biomass during conversion processes[24], where cross-linking and connectivity between lignin and polysaccharides makes depolymerisation or pre-treatment of biomass challenging[17,22,25].

Several strategies have been explored to separate lignin while leaving the cellulose component intact, or to decompose lignocellulose and its polysaccharide components into accessible monomers (Fig. 3, Lignocellulosic). This includes physical methods, such as ball-milling (grinding process aided by balls through impact and attrition inside a rotating cylindrical shell) and extrusion (deconstruction process involving high shearing forces typically enabled by rotating screws), which work by reducing particle size, increasing porosity and disrupting cross-linking. Conversely, thermal methods, such as microwave heating, aid decomposition by swelling and fragmenting the polymeric chains, making them susceptible to hydrolytic reactions[26,27,28]. Chemical methods typically involve the use of acids, alkali or organic solvents during pre-treatment[22,29], but saline conditions, such as acidified metal salt hydrates have also been reported to depolymerise cellulosic biomass into water-soluble oligomers, primarily glucose[30,31]. Other chemical methods include the use of deep eutectic solvents (solvents having a lower melting point than their constituents) to preferentially dissolve lignin, leaving behind purified cellulose, or fractionation techniques that use solvents or ionic liquids to convert cellulose and hemicellulose to furfurals and levulinic acid[25]. In general, a combination of one or more physical, chemical, thermal or biological approaches increases pre-treatment efficiency and methods with yields of >99% have been demonstrated[17,22,32]. For example, mechano-catalytic deconstruction of cellulose uses catalytic amounts of acid during ball-milling followed by hydrolysis at 130 ºC to fully convert the substrate to water-soluble glucose and xylose within 2 h[33].

Another widely-adopted approach for deconstructing biomass is through combination of mechanical, thermal or chemical processing with enzymatic hydrolysis to simpler sugars[22]. Enzymes such as cellulases (extracted from the fungus *Trichoderma reesei*)[34], β-glucosidase and xylanase are the most commonly used enzymes for lignocellulose pre-treatment[35]. Cellulosomes, multi-enzyme extracellular complexes used by bacteria to decompose cell wall material, have also been investigated for abiotic cellulose deconstruction[36]. Finally, catalytic depolymerisation of lignocellulosic components has also gained ground in recent times with a variety of solid heterogenous catalysts based on Pt, Ni, and other metals demonstrating the conversion of cellulose to glucose and polyols through a combination of hydrolysis and hydrogenation (> ~1 MPa H_2) steps at elevated temperatures (> 100 °C)[37,38]. Lignin depolymerisation to aromatics using transition metal-based catalysed C–C and C–O bond cleavage has also been reported[24,39]. Besides these, several electrochemical lignin conversion approaches have been studied, mostly in alkaline media, and shown to proceed via oxidative or reductive C–C or C–O cleavage yielding aromatic compounds[40].

In addition to plant-based, lignocellulosic substrates, biomass also includes meat or diary-based food waste containing proteins and fats[41]. Several different approaches have emerged for extracting proteins from animal tissues such as aqueous phase extraction, denaturing and non-denaturing extraction[42]. The depolymerisation of proteins into various hydrolysates can be achieved using chemical (acid or alkaline), enzymatic (proteases) or microbial pre-treatment methods[43]. Fats, on the other hand, are typically hydrophobic and therefore more challenging to break down into water-soluble components[16]. Enzymatic hydrolysis or fungal autolysis, in combination with microbial fermentation, has been used for converting mixed food waste to simpler, water-soluble molecules[44]. For example, bakery waste has been used for the production of glucose (via hydrolysis using enzymes produced from *Aspergillus awamori* and *Aspergillus oryzae*), followed by *Actinobacillus succinogenes* fermentation yielding succinic acid, which can serve as an important intermediate to produce valuable chemicals[45,46]. Hydrothermal oxidation has also recently been shown to convert simulated mixed food waste, including tissue materials, to formate and lactate which may be recovered and used as platform chemical, or used in further conversion processes[47].

[H2] Plastics

Plastics consist of a wide range of synthetic solid materials and present a critical challenge for conversion as they have robust polymeric structures with different chemical compositions, some of which are highly recalcitrant to decomposition. Plastics can broadly be categorised into ‘condensation polymers’, having carbon-heteroatom (C–X, where X = O, N) linkages (such as polyesters, polyamides) and ‘addition polymers’ having sp^3-hybridised C–C backbones (such as polyolefins)[17,48]. Condensation polymers are comparatively easy to cleave into constituent monomers with polar functional groups[48] and chemical pre-treatment with acids and alkali are commonly used to enable their depolymerisation by hydrolysis (see Fig. 3, Plastics)[49,50]. For example, polyethylene terephthalate (PET) can be hydrolysed to its building blocks, ethylene glycol and terephthalic acid, using acid or alkaline pre-treatment in moderate to high temperature ranges (40–80 °C)[50]. Similar strategies have also been used to break down plastics like polylactic acid (PLA), polyurethane (PUR) and polycaprolactone (PCL) to water-soluble carboxylic acid and alcohol species[51-53]. Polyamides such as nylon are resistant to alkaline conditions, but more prone to acid hydrolysis[54]. Besides hydrolysis, cleavage of plastic C–X bonds can be achieved by alcoholysis[55], glycolysis[56], ammonolysis[57], or aminolysis[58] by adding the plastic to the appropriate solvent system at various temperatures. Catalytic hydrogenation using Ru or Ir-based organometallic catalysts have been explored recently as an atom-economical approach to deconstruct nylon, PUR and PLA to smaller polyols and amines[59-61].

Biological approaches (enzymes and microbes) have also been demonstrated to facilitate degradation of condensation polymers[62]. Hydrolytic enzymes such as cutinases (for example, leaf compost cutinase), lipases, and esterases (for example, PETases) have been shown to degrade PET into smaller oligomeric and monomeric fragments under aqueous or semi-aqueous conditions[62]. Cutinases are also active in cleaving the amide linkages present in polyamides[63]. Some of these enzymes have been isolated from bacterial strains that demonstrate direct microbial breakdown of plastics, for example *Ideonella sakaiensis* that utilises waste PET as its carbon source by secreting the hydrolytic enzymes PETase and MHETase to convert the polymer into usable ethylene glycol and terephthalic acid[64]. A recent demonstration also revealed a fermentative metabolic pathway in *Ideonella sakaiensis* enabling PET degradation to ethanol and acetate under anaerobic conditions[65].

Similarly, there are reports on several ‘plastic-eating’ fungi species such as *Aspergillus tubingensis* that can break down PUR[66]. A combination of these techniques offer alternative approaches to use condensation polymers by breaking them down into accessible monomers.

Addition polymer plastics (for example, polyethylene (PE), polystyrene (PS), and polypropylene (PP)), on the other hand, are extremely challenging to deconstruct under mild or aqueous conditions[17,48]. Recent developments towards more efficient degradation include microwave-assisted or hydrothermal oxidative depolymerisation using oxidising agents (such as nitric acid and nitric oxides) for PE breakdown, producing simpler carboxylic acids (such as succinic acid and glutaric acid) under aqueous conditions[67,68], and metal catalysts based on Co, Mn, Zr and V for the depolymerisation of PE and PS under aerobic conditions in water or acetic acid media[69]. Recent reports also demonstrate light-induced, acid-catalysed, aerobic deconstruction of PS to products such as benzoic acid, acetophenone and formate with high selectivity[70,71]. Besides the oxidative approaches which impart functionality to the depolymerised monomers, hydrogenolysis and catalytic cracking has been extensively used to convert polyolefins (such as PE, PS and PP) to shorter hydrocarbons, but these products are relatively inert and mostly gaseous, and therefore not ideal as feedstocks for waste-to-chemical technologies[48,72]. Chloroaluminate ionic liquids have also been used recently to convert PE and PP to liquid isoalkanes (C_6–C_{10}) at temperatures below 100 ºC[73]. While some species of bacteria and fungi are known to degrade polyolefins over time by secreting enzymes, these biocatalytic processes demand further research to improve efficacy and yields on a commercial scale[74].

[H2] Industrial by-products and CO_2

Although biomass and plastics are major focus points from the perspective of MSW mitigation, other substrates found in industrial effluents may also be directly used as feedstock for waste-to-chemical processes (Fig. 3, Industry Effluent). A few examples include glycerol, which is a by-product of biodiesel and soap industries[75], ethylene glycol from PET manufacturers or aircraft de-icing wastes[76], and various carbohydrate fractions from pulp-mill wastewaters[77]. While the sole photocatalytic degradation of pollutants from aqueous bodies (for instance, organic contaminants found in industrial wastewaters) does not create value-added products, the solar-powered utilisation of pollutants to produce fuels like hydrogen or other valuable chemicals would qualify this process to fall within the scope of solar reforming[78]. Airborne waste streams such as CO_2 emitted from various industrial sectors may also be an attractive feedstock for waste-to-chemical technologies[79-81]. The CO_2 (from compressed sources, flue-gas or direct air capture) can be reduced to products such as syngas, formate, or alcohols and be coupled to the oxidation of solid waste streams, thereby generating useful carbon-based organic products from both half reactions (Fig. 3)[82-85]. Despite the large volume of research on CO_2 reduction (CO_2R) systems and significant advances in the past decade, a vast scope of development is still required to integrate CO_2R technologies (to products such as CO, syngas, formate, alcohols, hydrocarbons) with the utilisation of pre-treated solid waste streams.

[H1] Fuel and chemical production strategies

There are many examples of light-driven reactions where photons are captured to convert waste or waste-derived materials into products of economic value. Such ‘photoreforming’ reactions are typically driven by high energy photons (UV or near-UV) using photocatalysts such as TiO_2[86], but also by artificial irradiation such as blue light-emitting diodes[71]. By contrast, the solar spectrum is primarily low-energy photons with UV only accounting for 3.7% of irradiance (Fig. 2). By designing devices and processes that capture energy from the wider solar spectrum, the performance and efficiency of solar reforming can be improved. This will enable solar reforming driven by photons (solar catalytic reforming) and heat (solar thermal reforming)[87]. For example, solar concentrators can be integrated with solar reforming devices to achieve higher temperatures, catalytic rates, and chemical production rates[88].

The reduction half reaction in solar reforming can be tailored to a specific application (such as hydrogen evolution reaction (HER) or CO_2R). It is most often employed for green hydrogen production where solar reforming can be considered a catalytic process somewhere between water-splitting and organic photo-redox catalysis. In this system, the oxygen evolution reaction (OER) is replaced by the oxidation of organics derived from waste[89], avoiding the high energy demand and sluggish kinetics that cause the key bottleneck during the thermodynamically challenging water splitting rection ($\Delta G^o = +237$ kJ mol^{-1}; $E^o = 1.23$ V vs. the reversible hydrogen electrode [RHE] at 25 ºC)[16]. Oxidation of waste-derived substrates such as alcohols, sugars, or aldehydes substantially lowers the energy barrier; solar reforming of glycerol ($C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$; $\Delta G^o = +5$ kJ mol^{-1}, $E^o \approx 0$ V vs. RHE) or ethylene glycol ($C_2H_6O_2 + 2H_2O \rightarrow 5H_2 + 2CO_2$, $\Delta G° = +14$ kJ mol^{-1}, $E^o \approx 0$ V vs. RHE) enables oxidation over valence band holes with less driving potential (E^o) compared to water splitting[16,90].

The potential of using waste-derived substrates for fuel production can be estimated through complete sunlight-driven conversion of model substrates under aqueous conditions[90]. For example, one mole of glucose ($C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$, $\Delta G° = -35$ kJ mol^{-1}) or ethylene glycol can unlock twelve or five moles of H_2, respectively[90]. Therefore, assuming 100% conversion of cellulose to glucose (~45% fraction of ~4 Gt yr^{-1} lignocellulosic biomass residue produced globally)[21], ~240 Mt of 'green' hydrogen can be generated annually via solar reforming processes. Similarly, the ethylene glycol monomers from ~32 Mt yr^{-1} of PET plastic wastes generated worldwide can yield ~1.2 Mt yr^{-1} of green hydrogen[16]. These numbers are encouraging considering current global hydrogen demand was around 90 Mt in 2021[91]. Supplemented with an additional 1.5 Gt yr^{-1} lignocellulosic biomass from natural detritus (~1% of annual production) would allow solar reforming to cover global hydrogen demand (~320 Mt yr^{-1} in 2050)[92] using biomass alone.

[H2] Metrics for solar reforming

It is important to consider suitable performance metrics for evaluating different solar reforming technologies and assessing their viability for commercial implementation. The most common metric in artificial photosynthesis is the solar-to-fuel conversion efficiency (η_{STF}) as shown in eq. (1), where r_{SR} is the rate of product formation by solar reforming, ΔG_{SR} is the change in Gibbs free energy during solar reforming, P_{total} is the total light intensity flux and A is the area of sunlight irradiation:

$$\eta_{\mathrm{STF}} = \frac{r_{\mathrm{SR}}\ (\mathrm{mol \cdot s^{-1}}) \times \Delta G_{\mathrm{SR}}\ (\mathrm{J \cdot mol^{-1}})}{P_{\mathrm{total}}\ (\mathrm{W \cdot m^{-2}}) \times A\ (\mathrm{m^2})} \tag{1}$$

This definition relies on the ΔG value from the reforming reaction and therefore reflects the amount of energy from the reforming reaction stored in the product. For solar reforming processes, the low ΔG values involved (ΔG ~0 kJ mol^{-1}), generate a η_{STF} that is, per definition, very low (~0%) even if the quantum yield and therefore product formation rate is very high (Fig. 4)[93]. Thus, this efficiency metric does not consider the total energy stored within the fuel as utilisation produces more thermodynamically stable chemical compounds (that is, H_2O and CO_2). Use of the chemical fuel product (for example, H_2) can therefore yield significantly more energy than the solar energy used in the reforming reaction. Substituting ΔG_{SR} for $|\Delta G_{\mathrm{use}}|$ (the energy released from using the fuel) can express the process efficiency from the perspective of human-engineered transformation of solar energy to heat or electricity (Fig. 4). This is made possible by relying on natural photosynthesis to convert combustion products (H_2O, CO_2) back into energy-rich reformable substrates (such as biomass), then using solar reforming as a low-energy step to produce the fuel. In the case of artificial photosynthesis, where all stages of fuel production are achieved (for example, CO_2R directly to fuel), the efficiency considering the energy value of the fuel product would be a true representation of the process' ability to store accessible energy. Furthermore, the traditional η_{STF} definition does not account for the energy required for substrate pre-treatment in a solar reforming process. Considering the significant influence of substrate choice on the Gibbs free energy and thus η_{STF}, a more consistent and technologically relevant metric for solar reforming (and solar chemical technologies generally) is the areal activity or production rate (r_{areal}). This metric gives the molar amount (n) of product formed per unit area of sunlight irradiation (A), per unit time (t), as shown in eq. (2)[93]:

$$r_{\text{areal}} = \frac{n_{\text{product}}\ (\text{mol})}{A\ (\text{m}^2) \times t\ (\text{h})} \tag{2}$$

However, r_{areal} does not consider the type of waste being mitigated or fuel being generated. To account for the nature of substrate and products, the economic value creation from solar reforming, a metric we call the solar-to-value (STV) creation rate (r_{STV}), is defined in eq. (3), where C_i and C_j are the costs of chemical i and substrate j, respectively, $C_{pt,j}$ is the cost of pre-treatment for substrate j, and n_i and n_j are the amounts of chemical i produced and substrate j consumed, respectively:

$$r_{\text{STV}} = \frac{\sum_{\text{i}=1}^{\text{n}} C_{\text{i}}\ (\text{£ mol}^{-1}) \times n_{\text{i,product}}\ (\text{mol}) - \sum_{\text{j}=1}^{\text{m}} (C_{\text{j}} + C_{pt,\text{j}})\ (\text{£ mol}^{-1}) \times n_{\text{j,substrate}}\ (\text{mol})}{A\ (\text{m}^2) \times t\ (\text{h})} \tag{3}$$

The r_{STV} can also be further expanded to include scaling factors, product separation and other process costs during practical deployment, making it a robust and adaptable process value metric for solar reforming that encompasses a wide range of products, substrates and deployment architectures[93]. In particular, pre-treatment costs may have an outsized influence on the r_{STV}, but this is strongly dependent on the cost and energy-requirement of the pre-treatment process. Previous analyses determined that an alkaline hydrolytic pre-treatment of condensation polymers dominated the economic viability of a pilot-scale PC reforming plant despite significant base recovery and reuse[16]. The cost of novel pre-treatment methods must therefore be carefully considered in the development of solar reforming as a sustainable and economical industrial process. The r_{STV} also fluctuates with market prices of chemicals consumed (for instance, by creating value from waste mitigation such as carbon-tax and waste gate-fees or disposal costs) and generated (fuels or chemicals from redox processes), but overall better reflects the economic value of the process. It is also more comparable with other chemical production processes than the traditional η_{STF} used in artificial photosynthesis, where only negligible value can be sourced from substrate consumption and oxygen evolution.

Solar reforming is both a sunlight-driven and catalytic process, therefore system performance is tied to the photophysical properties of the semiconductor light-absorber as well as the electronic and chemical properties of the catalysts[94]. Catalyst and light-absorber development are therefore equally important to applied solar reforming and the selection, screening, characterisation and optimisation of different catalysts and co-catalysts can be aided by electroanalytical methods prior to integrating a particular catalyst with a solar reforming system. Furthermore, the design of solar reforming systems has an enormous impact on the efficacy and possible applications of the process, and can be grouped into three architectures: Photocatalytic (PC) reforming, photoelectrochemical (PEC) reforming and photovoltaic-electrochemical (PV-EC) reforming (Fig. 2).

[H2] Photocatalytic (PC) reforming

PC reforming involves the use of homogeneous or heterogeneous semiconductor photocatalysts that use solar energy to directly catalyse the underlying chemicals reactions.[95] Homogeneous photocatalysts have the potential advantage of directly interacting with polymeric substrates, thereby avoiding the need for pre-treatment in some cases[96,97]. Upon solar illumination and subsequent generation of electron-hole pairs in the photocatalyst (Fig. 5a), the holes (in the valence band (VB)) can oxidise organic substrates, ideally derived from waste feedstocks, into useful chemicals. The electrons (in the conduction band (CB)) drive HER or CO_2R[16,90]. This is possible when the VB of the photocatalyst is more positive relative to the oxidation potential of the particular substrate, while the CB is more negative than the reduction potential of HER (or CO_2R)[16,90]. Using waste derived oxygenates also reduces charge recombination in the photocatalyst by rapidly scavenging holes, thereby increasing the hydrogen production rate[16]. Selecting appropriate substrates can also lower the energy barrier and oxidation potential for the overall process, allowing a wider range of small band-gap semiconductor light absorbers to be considered. The use of co-catalysts can further accelerate the process through improved charge extraction and kinetics[95]. For example, CB electrons can be transferred to hydrogen evolution co-catalysts such as Pt, Pd, or Ni to improve hydrogen yield[19,95], or to different molecular or biological co-catalysts that perform CO_2R under aqueous conditions, thereby broadening the fuel scope (Fig. 5a,b)[82,98]. The detailed mechanistic steps are shown in Fig. 5b.

The simplest configuration for PC reforming involves aqueous 'one-pot' particle suspensions, where the photocatalyst and co-catalyst are dispersed in a reaction medium containing pre-treated substrates[95]. This gives the benefit of high surface area and good mixing, allowing efficient mass transfer between substrate and (co-)catalyst species, as well as ease of application. A range of photocatalysts have been reported for reforming reactions using this approach[18]. Among these, TiO_2 (in combination with a co-catalyst), has by far been the most commonly studied light absorber for producing hydrogen[99]. Various $TiO_2|M$ (M = Pt, Cu, Pd, Au, Cu_2O, among others) combinations have been evaluated for PC reforming of model compounds (such as saccharides and alcohols) as well as chemically and/or mechanically pre-treated biomass substrates such as microcrystalline cellulose, paper, and various plant matter[100-102]. Plastics pre-treated under strong alkaline conditions such as PVC, nylon, PE, PET and PLA have also been investigated as feedstocks for hydrogen production using $TiO_2|Pt$ photocatalysts[101,103]. While TiO_2 absorbs in the UV region ('photoreforming') and usually requires a co-catalyst to drive the PC reactions, other materials such as CdS quantum dots absorb visible light ('solar reforming'), do not require a HER co-catalyst and behave as soluble (homogenous) catalysts under aqueous conditions[96]. CdS has been employed for PC reforming of biomass (cardboard, α-cellulose, wood branch, lignin, food waste)[96,104,105] and plastics (PET, PLA, PUR) under alkaline conditions (required for waste pre-treatment and CdS stabilisation via oxide passivation)[103] at room temperature with high yields.

More recently, visible-light absorbing carbonaceous photocatalysts such as carbon-nitrides (CN_x) and carbon dots (CDs) have been introduced as non-toxic candidates for the PC reforming process due to their low cost and scalable production from simple organic precursors or even cellulosic waste[99,107,108]. Various forms of CN_x combined with different co-catalysts (for example, Ni_2P, Pt, MXenes, $Ni[(P_2N_2)_2]^{2+}$ (NiP)) have been used for PC reforming of biomass-derived substrates including cellulose, xylose and hydroxymethylfurfural (HMF)[107,109-111], as well as alkaline pre-treated food wastes (apple, bread, cheese)[104], under aqueous conditions. Alkaline pre-treated plastics have also been employed for PC reforming using CN_x[112,113]; for example, PC reforming of PET and PLA were carried out using cyanamide functionalised CN_x with Ni_2P co-catalyst ($^{NCN}CN_x|Ni_2P$) under alkaline conditions to generate hydrogen[112], and $^{NCN}CN_x|Pt$ was able to solar-reform di-carboxylic acids obtained from PE pre-treatment into alkanes and hydrogen gas[114]. The PC reforming of biomass under acidified high-saline conditions ($LiBr+H_2SO_4$) has also been demonstrated using $^{NCN}CN_x$ $|Pt$[115]. CDs have so far been used for PC reforming of biomass components under benign aqueous conditions with molecular co-catalysts, such as NiP[97]. Other photocatalysts less commonly investigated for PC reforming producing hydrogen include covalent triazine frameworks[116], ZnS[117], ZnCdS[118] and graphene oxide dots[119], which make use of various oxidation substrates. Apart from generating hydrogen as a product, PC reforming systems can also drive other reduction reactions. Recent demonstrations showed the coupling of CO_2R with PC reforming of enzymatically (cellulase) pre-treated cellulose on TiO_2 integrated with a catalyst such as a molecular co-catalyst or a CO_2 reducing enzyme (formate dehydrogenase, abbreviated as FDH)[82,98]. Another study reported the use of layered Nb_2O_5 photocatalyst for converting plastics (PE, PP and PVC) to C_2 fuels via a two-step photo-oxidation followed by photo-reduction process[120]. Recently, a new chemoenzymatic pathway has been introduced allowing PC reforming of polyester plastics (PET, PCL) and nanoplastics to operate under mild conditions (as opposed to harsh alkaline conditions under elevated temperatures) with enzymatic pre-treatment (pH 6–8, moderate temperatures)[121]. In addition to offering a more sustainable and cost-effective approach to hydrogen production (with TiO_2|Pt and CN_x|Ni_2P photocatalysts), the mild conditions used for chemoenzymatic PC reforming also allowed photocatalytic CO_2-to-syngas production (with TiO_2|CotpyP) coupled to plastic upcycling[121].

For economical, scaled application of solar reforming technologies, catalyst or device lifetime is a critical consideration that can outweigh the production cost of the material or device itself, and is the second most important factor in achieving low energy payback times (behind production rates)[16,122]. The economic feasibility of hydrogen fuel production from PC or PEC processes (non-reforming) has been theorised under the assumption that the catalyst components have lifetimes of 7–20 years[123,124], and in the context of solar reforming, catalyst or device lifetimes exceeding 1 year are critical[16]. To this end, development of robust, reusable PC reforming materials is of particular interest, including floating photocatalysts[125], photocatalyst sheets[93,113,114], and magnetically recoverable photocatalysts (Fig. 5c,d). Such catalyst immobilisation unlocks additional advantages such as easy retrieval and reuse, and PC reforming of non-transparent waste streams[113,125].

Immobilisation has not yet been extensively investigated in the context of solar reforming, but photocatalyst sheets for hydrogen generation from water splitting have been reported. These sheets facilitated the scalable application of photocatalysis with minimal loss in activity compared to the powdered catalyst[126-128] and examples of photocatalyst sheets for water treatment have been extensively reported[129,130]. In transparent solutions, the reaction rate and quantum efficiency of immobilised photocatalyst sheets is generally lower than photocatalyst powders deployed as a slurry due to lower interfacial area available for PC reactions[131] and reduced external mass transfer from increasing diffusional lengths to bring reactants from the bulk solution to the catalyst surface[132,133]. Such decreased kinetics can be mitigated through careful film design, such as achieving sufficient thickness to maximally absorb incident light and sufficient film porosity to afford a large interaction area[134]. Selection of support materials can also mitigate production rate bottlenecks, for example immobilisation of the photocatalyst on fixed bed materials such as high surface area silica rather than a flat glass panel to increase interaction area[135,136].

Other common approaches for catalyst reuse, mostly in the context of water treatment, include immobilisation on floating support materials and integration with magnetic nano- or micro-particles that allow slurry catalyst deployment with a facile and rapid recovery process (Fig. 5c)[137,138]. Recently, magnetically separable graphitic CN_x materials have been demonstrated in oxidative water treatment applications coupled with transition metal ferrites (for example, $CoFe_2O_4$, $NiFe_2O_4$) as the magnetic material to form heterojunctions which enable new reaction pathways in addition to facilitating rapid catalyst separation and reuse[139,140]. However, the majority of such magnetic photocatalyst systems have only been demonstrated at lab-scale and challenges associated with scaling still persist, despite promising efforts being made to explore large-scale options[141]. Floating CN_x materials using cellulose foams, expanded perlite, porous glass beads, and melamine sponge as supports have also been a subject of recent investigation and show facile gravimetric separation of the CN_x catalyst as well as oxidative degradation of various toxins and inhibition of bacterial growth[142-145]. Examples of floating PC systems include deposition of CN_x on hollow glass microspheres, followed by a Ni_2P or Pt co-catalyst, showing successive production of hydrogen and rapid catalyst separation and recovery over multiple trials[125], and the integration of floating TiO_2 and with an enzyme (FDH) co-catalyst for PC reforming of cellulose coupled to CO_2R[98]. Though few examples of photocatalyst immobilisation for PC solar reforming exist in the literature to date, many of the immobilisation and separation techniques for water splitting and water treatment applications are immediately transferrable to solar reforming.

Despite the wide scope and extremely flexible deployment of PC reforming, there are certain limitations to this process. First, current PC reforming approaches for hydrogen evolution suffer from low areal activity with low product and value creation rates (Table 1), and estimates suggest that PC reforming performance must be increased at least 50 fold to achieve economically viable green hydrogen production[16]. The reasons for such poor performance include high carrier recombination rates despite the presence of co-catalysts, poor substrate-photocatalyst interaction, wide band-gaps, insufficient light absorption, low conductivity and catalyst deactivation[146,147]. Another major general limitation of PC reforming is the poor selectivity of oxidation products owing to the difficulty and complexity of co-catalyst design compatible with powder synthesis techniques and for application in a single substrate solution (Table 1). During typical PC reforming of waste-derived substrates, a mixture of various organic end-products and by-products are formed in solution via non-selective photo-oxidation that are extremely challenging to separate and therefore hold little commercial value[16]. Such non-selective oxidation results from uncontrolled adsorption-desorption of intermediates, *in-situ* generation of oxidising radicals (such as $^{\bullet}OH$, $^{\bullet}O^{2-}$) and product saturation leading to over-oxidation[18,148]. Furthermore, substrate over-oxidation often leads to an undesirable end-product of CO_2, thereby increasing the carbon-footprint of the overall process and decreasing the purity of the produced fuel (though the CO_2 can be trapped in solution as CO_3^{2-} under alkaline conditions)[18].

Overall, PC reforming is a low cost, versatile, and simple technique that lends itself to decentralised deployment; PC materials require very little hardware beyond a suitable enclosure, meaning they can be easily applied to small systems or in remote locations without significant capital investment. Catalyst immobilisation can help address catalyst recovery and reuse, and application in turbid waste solutions. However, drawbacks of such PC systems include low production rates and difficult design, optimisation, and improvement of the individual oxidation and reduction processes since both half reactions must be performed under the same solution conditions.

[H2] Photoelectrochemical (PEC) reforming

Unlike PC systems where both half reactions occur proximally on a photocatalyst particle, PEC systems rely on separated (photo)electrodes that are electrically connected using a wire. Photoelectrodes consisting of a photo-absorber (semiconductor) with additional conductive layers and/or catalysts absorb light and catalyse oxidation or reduction processes (Fig. 6a,b). They are submerged in solution (electrolyte) and often need an external bias in addition to the energy derived from solar irradiation for operation. Typical PEC systems have two photoelectrodes separated into two compartments, allowing for spatial separation of the redox half-reactions and product formation (Fig. 6c, d). In this way, many of the current shortcomings of PC reforming can be addressed using PEC systems[94,149]. Most importantly, the selection of materials is much more flexible owing to the separation of the reactions and device engineering, allowing for highly selective redox catalysts to be coupled with efficient light absorbers. Furthermore, this separation enables independent development and study of catalysts for one half-reaction without affecting the other half-reaction. The solution conditions in each chamber can also be tailored to the oxidation or reduction reaction. Under certain configurations these benefits can outweigh the cost and complexities associated with PEC fabrication.

Recently, photoelectrodes inspired by the architecture of photovoltaic cells have been developed as integrated light-absorbers that employ electron and hole transporting layers to efficiently extract the photo-generated charge carriers and prevent recombination. These structures improve the photocurrent density, onset potential and performance (Fig. 6c-e)[150,151]. PEC reforming can therefore make use of state-of-the-art photovoltaic materials to improve rates and activities. For example, light-absorbers with high absorption coefficients in the visible region, such as halide perovskites, are promising candidates for fabricating photoelectrodes and can provide high rates of product formation[152,153]. Although perovskites are sensitive to moisture, the recent emergence of robust encapsulation strategies has allowed for their use under aqueous conditions[150,151,153,154]. Other photovoltaic devices such as conventional silicon panels can also, in principle, be integrated into the

PEC architecture[155]. Moreover, PEC assemblies can also benefit from harvesting heat (IR) using thermoelectric modules to enhance the reaction kinetics in solution, thereby improving PEC reforming performance[156,157].

For practical solar reforming, PEC assemblies can function efficiently with a single light absorber and operate without externally applied bias or voltage. Consequently, photoelectrode light-absorption efficiency and area play a vital role in device efficacy. PEC systems can also draw inspiration from PC reforming by integrating useful photocatalysts (for example, CN_x) into robust electrodes[158]. Typical PEC cells couple water-splitting or CO_2R with OER and therefore require an external bias[159-161], or two light-absorbers connected in tandem to drive the overall process[85,150,154,162-167]. By replacing OER with less thermodynamically demanding oxidation of waste-derived substrates (Fig. 6a, b), PEC reforming can be performed efficiently under bias-free conditions with a single light-absorber (Fig. 6c-e)[168]. Although a few PEC systems have also reported oxidation of model waste compounds such as glycerol, glucose and HMF at the anode using dual light-absorber tandems analogous to artificial photosynthesis systems, the second light-absorber is not required in solar reforming from a thermodynamic point of view (see above), and may ultimately even limit the potential for practical implementation[169-172].

The use of real-world waste streams in a single-light absorber PEC arrangement without external bias is thus desirable, and several recent examples have achieved this goal through coupling waste oxidation with HER or CO_2R (Fig. 6c-e)[83,149,173,174]. A bias-free $Cu_{30}Pd_{70}$|perovskite|Pt PEC arrangement demonstrated reforming of different waste substrates to green hydrogen with production rates 2-4 orders of magnitude higher than those observed in PC processes (Tables 1 and 2)[149]. This device also demonstrated high selectivity (60–90%) in converting waste streams such as mechanochemically pre-treated PET bottles and cellulose to glycolic acid and gluconic acid, respectively[149]. PEC devices also offer the benefit of modular configurability and two different arrangements were demonstrated with the bias-free $Cu_{30}Pd_{70}$|perovskite|Pt system: a two-compartment, two-electrode configuration and an integrated, single-compartment 'artificial leaf' (Fig. 6e). The two-compartment arrangement allows for process and catalyst optimisation (Fig. 6b), substrate diversification and reforming of non-transparent waste streams at the dark electrode. The standalone 'artificial leaves' are useful for their compactness, easy retrieval and reuse, and portability (Fig. 6e)[149,167]. PEC systems have also demonstrated selective CO_2R to fuels using single-light absorber perovskite-based photocathodes while simultaneously reforming PET plastic to glycolic acid at the anode without external bias[83]. Depending on the type of catalyst integrated in the photocathode, different CO_2R products were obtained, including CO (using molecular a Co-based catalyst), syngas (using a bimetallic Cu-In alloy) and formate (using a biological enzyme catalyst) with high selectivity[83]. The versatility and performance of the single light absorber PEC arrangement subsequently also enabled the integrated capture (using capturing agents like amines or hydroxides) and solar-driven conversion of CO_2 from dilute sources such as flue gas and air, coupled to PET reforming[84]. This operation of the unique system was possible owing to the replacement of water oxidation with thermodynamically less demanding pre-treated PET oxidation.[84]

These PEC reforming systems, under unassisted conditions (that is, powered only by sunlight without external bias), generate controlled activity at the respective electrodes, governed by the open-circuit voltage (V_{oc}) from the light absorber, the efficiency of the catalysts and the pH of the medium[154,168]. Thus, tuned activity can be achieved by changing these variables during PEC system development to achieve product selectivity at the respective electrodes for enhanced valorisation. These versatile new systems in the domain of solar reforming therefore have the potential to push the boundaries and reach high fuel and chemical production rates and product selectivity (Table 2).

[H2] Photovoltaic-electrochemical (PV-EC) reforming

PV-EC technologies use electricity generated from photovoltaic panels to drive an electrolytic reforming reaction (Fig. 6f)[178]. Since the overall process can be powered solely by sunlight, highly efficient PV-EC setups can be adopted for solar reforming, despite their higher system and operational complexity compared to PC and PEC architectures[94,179]. Since the light absorption component of PV-EC systems is completely separated from the electrochemistry, the choice and optimisation of electrocatalyst(s) becomes critically important and may be useful to guide the development and selection of materials for other reforming devices.

Most electrolysers reported in the literature or commercially deployed are based on those used for overall water splitting or CO_2R (with OER as the anodic reaction)[94,179], but electrolysis setups that utilise waste streams as feedstocks are now under growing development[114,180-183]. For example, electrolysers with transition metal-based anodes have been reported to valorise pre-treated PET and simultaneously generate hydrogen or reduce CO_2 at the cathode[180,181]. Carbon-based anodes can produce useful alkenes (ethylene and propylene) from chemically pre-treated PE plastics[114] or biologically pre-treated (using bacteria and fungi) food waste (the latter process has been termed as 'bio-electroreforming')[46]. A high-entropy alloy (HEA-CoNiCuMnMo) has been used to electrochemically valorise glycerol to formate with accompanied hydrogen production[184] and other electrochemical oxidation approaches have been used to valorise lignin into platform molecules[24,40].

The use of sunlight to drive such waste electrolysis cells is an attractive option considering the high product formation and value creation rates that can be achieved depending on the catalyst(s) and photovoltaic cells employed. However, direct comparison with other solar reforming approaches can be difficult since most demonstrations of PV-EC systems are connected to commercial solar panels but only report current densities or rates over the electrode area, rather than the solar collection area. For example, a recent report detailing PV-powered electro-reforming of chitin demonstrated hydrogen production of 73 mL min^{-1} (~180 mmol h^{-1}) using an electrode area of 28 cm^2, but only specified the use of three 50 W photovoltaic panels without reporting the irradiation area[185]. For accurate comparison between different types of solar reforming architectures, a consistent metric of solar areal production should be adopted and irradiation areas should be reported.

[H2] From atom to photon economy

The concept of 'atom economy' in organic synthesis has long been prevalent with sustainable research activities, aiming to reduce waste by incorporating all atoms of a substrate in the desired product[186]. In addition to a full, 'atom economic', conversion of the waste substate into products, a solar reforming reaction should also make use of all photons to maximise rate of product formation and thus value creation. The light absorber of an ideal solar reforming system should absorb UV and visible light photons with maximum quantum yield to generate as many charge carriers as possible. Both charge carriers (electron and holes)[89,187] should be used to drive the individual redox half reactions (waste oxidation and reductive fuel production) at maximum rate. Heat, generated by the remaining non-absorbed low-energy (IR) photons, and from thermalisation losses from absorbed high-energy photons, can be employed for waste pre-treatment or improve the rate of catalytic reactions. Integration of thermoelectric modules to systems such as PEC devices provides an opportunity to establish a temperature-gradient to provide additional energy (voltage) to the solar reforming process, which can further increase the rate of catalytic substrate conversion. Additionally, solar reforming can also be coupled to thermal water desalination applications to produce freshwater[188,189]. The creation of maximum value will therefore be established when a solar reforming process delivers full atom and light management. Thus, maximum value in solar reforming can be achieved by expanding the concept of an 'atom economy' to include a 'photon economy', which should motivate work on light and thermal management, and full spectral utilisation[88].

[H1] Conclusion and outlook

Though solar reforming is still in its development phase, the urgent need for green energy and waste remediation strategies demands consideration of all potential solutions. The case for solar reforming can be further argued by observing the growth trajectory of photovoltaics. Solar electricity generation using photovoltaics has received decades of industry-level development but was still considered a prohibitively expensive technology as recently as 15 years ago. Today, photovoltaics are among the cheapest forms of instantaneous electricity generation, though the challenges of storage (for example, batteries) and intermittent supply add complicated logistics and increase costs[190]. While solar electricity production is now mature and firmly established, solar-powered fuel and chemical production is still in its infancy with comparable growth potential. The effective implementation of scaled solar reforming will depend substantially on how it is deployed. Solar reforming technology (PC, PEC, or PV-EC) selection will depend on waste stream characteristics (substrate, turbidity, inorganic species), deployment location, and target products, while the overall capital and operational costs of such an installation will be affected by catalyst lifetime, viable pre-treatment methods, production rates and solar-to-value (STV) creation rates. Certain locations might benefit from smaller, low-cost, decentralised installations or plants for reforming relatively small and varied waste streams to produce hydrogen, for example biomass waste in a developing economy[191]. In this case, PC reforming might be a good option as it can operate in a contained system without complex reactor design and is naturally non-selective. A more concentrated, consistent waste stream with a specific desired product may instead opt for PEC or PV-EC to provide a specific oxidation potential and achieve higher product formation rates to keep pace with waste stream volume. Engineering improvements such as light management and concentration strategies may be applied to enhance performance through improved light harvesting and complementary light utilisation to boost reaction kinetics or drive multiple chemical processes[88,192,193].

[H2] Practical considerations

Challenges typically associated with solar photovoltaics, including sunlight intermittency, variability, and unpredictability, are (to some extent) mitigated through coupling solar energy harvesting directly to chemical processes. For PV, the electricity needs to be immediately directed into the power grid or else diverted to costly storage devices that are challenging to scale for seasonal energy storage (such as a battery). Furthermore, the nature of certain solar reforming systems, such as PEC and PV-EC, inherently allow for integration with other energy supplies, for example, conventional electricity that could buffer chemical production rates during low-sunlight periods as needed[194]. Although chemical energy storage presents these advantages over electricity storage, there are additional costs associated with building a solar-to-chemicals plant that buffers for intermittent demand. For example, process design and infrastructure must be sufficient to meet product demand (constant) from intermittent operational periods (during sunlight only), sufficient chemical storage is required to house this excess product until sale, and the daily operation cycle of a solar-to-chemical facility is complicated by daily start-up and shut-down, or transition from photoelectrocatalysis to electrocatalysis. Any sunlight-powered chemical production facility must therefore be built to gather sufficient energy to produce a fixed annual chemical load accounting for daily and seasonal variations in solar irradiance. For example, summertime production must buffer for constant demand in winter and daytime production must buffer for nighttime demand. Another foreseeable challenge for large-scale solar reforming plants is product collection across significant areas, adding substantially to infrastructure and operational costs. One possible mitigation strategy is solar concentration, thereby increasing the sunlight harvesting area and plant's chemical production rates but minimising the chemical production area and simplifying product collection. While this is not straightforward or inexpensive, any solar-energy harvesting facility will experience similar challenges and chemical storage solutions are well developed with minimal resource requirements or storage efficiency losses compared to equivalent technologies (such as batteries).

Additionally, catalyst and co-catalyst selection may need to be tailored to particular waste streams. For example, waste containing free sulfur compounds might poison Pt or Pd co-catalysts, requiring a co-catalyst not affected by the waste's specific chemistry, or additional pre-treatments to render the waste amenable to solar reforming. Outside of technical improvements, since half of solar reforming effectively operates as an advanced oxidation water treatment method, the economic case for solar reforming may also be improved by environmental policy related to discharging waste streams. For example, though a solar reforming system may not generate cost-competitive oxidation and reduction products alone, they may be subsidised by the 'gate-fee' for accepting and disposing the waste stream, creating niche market opportunities in the case of regulated waste.

Solar reforming offers attractive opportunities to increase sustainability and mitigate the environmental impact of the chemicals and energy industries. The key benefits include diverting waste from landfill and incineration, reducing demand for fossil fuel feedstocks, and green production of fuels such as hydrogen to reduce CO_2 emissions. Furthermore, solar reforming can facilitate localised fuel and chemical production, improving energy and resource security around the globe and providing affordable, clean energy. Nevertheless, the potential negative impacts of solar reforming also need to be considered if this technology is to play a significant role in the future chemicals and energy sectors. In particular, solar reforming requires substantial land usage to achieve the scale of areal solar collection necessary to achieve sufficient chemical production rates. However, open water sources may provide an opportunity for solar reforming applications. For example, PC reforming floaters or light-weight, floating PEC artificial leaves may be used in water-treatment facilities, lakes, ports, or dedicated pools[125,167]. Solar reforming may also contribute to some key environmental metrics such as eutrophication potential and mineral abiotic depletion potential, although these impacts are much more significant when relying on artificial irradiation or energy harvesting arrays (for example, wind turbines, photovoltaic panels) that use large quantities of mined resources in their construction. To this end, PC systems that can directly make use of solar irradiation for chemical conversion have a more environmentally favourable impact during their operation life cycle[195].

[H2] Future opportunities

In addition to the chemical pathways and implementation architectures discussed in this review, solar reforming can be applied more broadly to industrial photochemistry. Although we have focused on proton reduction (to hydrogen) and CO_2R as the reductive chemical pathways for solar reforming, in principle, any value-added organic transformation may be considered to replace such pathways[71]. For example hydrogenation of acetylene to ethylene using water as a proton source has been recently demonstrated as an alternative reduction pathway using carbon nitride as a visible light photocatalyst[196]. Solar reforming is also not restricted to operating under aqueous conditions. Although water-based chemistry is attractive from a sustainability standpoint, a wider range of photochemical organic transformations may be accessed by considering a variety of solvents (for example, biomass-derived solvents may be preferred[197]), particularly for PEC or PV-EC setups where the oxidation and reduction half reactions can be spatially separated and can be individually tuned. Finally, solar reforming may also be integrated with other recent advances in applied photochemistry or electrolysis, for example, photochemistry in flow which offer advantages in efficiency and scalability[113,198].

The solar reforming concept introduces an energy efficient use of both the oxidation and reduction half reactions in an integrated process powered by sunlight. By coupling useful reactions in both halves, multiple environmental concerns can be addressed in a single reaction, including waste mitigation, CO_2 utilisation, hydrogen production, and green synthesis of valuable chemicals. Furthermore, by taking advantage of organic oxidation processes, thermodynamically demanding water splitting reactions can be avoided. This improves the rate of hydrogen production over the status quo of overall water splitting while also avoiding the production of an explosive mixture of hydrogen and oxygen as well as removing the need for membrane product separation. Where prohibitively expensive sacrificial electron donors were previously required to enable chemical reduction reactions, now a range of possible alternative oxidation reactions with varying selectivity can be performed on waste substrates. By capitalizing on existing, energy-rich and abundant waste substrates, solar reforming gains an advantage over artificial photosynthesis in both value creation and thermodynamics of the underlying chemical reaction, providing an attractive medium-term route to commercialization of solar-to-chemical technologies. In the long-term, optimised artificial photosynthesis that can take CO_2 and H_2O directly to valuable chemicals will provide the greatest scalability and general use, and profit from industry knowledge pertaining to scaled solar reforming.

Integrating reforming into solar-powered redox processes takes a large step towards improving the sustainability of fuel and chemical production processes in circular chemical industries and could ultimately find large-scale applications in the form of solar-powered reforming plants or solar refineries. This approach is currently moving from the laboratory to relevant real-world demonstrations; for example all components in lignocellulosic biomass were recently valorised to useful products in conjunction with CO_2 upcycling by coupling solar reforming with other emerging sustainable technologies.[199] . In addition to continuously addressing fundamental research questions, the practical aspects of solar reforming are now becoming more dominant and require evaluation of effective, low-cost pre-treatment methods, catalysts and devices with long useable lifetimes, evaluation of reactor design and system scaling, integration of light and heat management strategies, and identification of niche markets for commercial validation are critical to enabling the success of this technology in the near future. Indeed, the essential role of sustainable waste-to-chemical technologies to produce fuel and chemicals in a future net zero economy is established and will rely primarily on CO_2, biomass and plastic waste (together >90%) as key carbon sources to replace fossil fuels[200]. Considering the need for clean fuel and chemical production from abundant waste streams and solar energy being the most abundant and cheapest energy form available, solar reforming is an obvious and well positioned emerging technology to support the transition from today's linear to a future's circular chemical industry.

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Author contributions

S.B. and E.R. conceived the design and structure of the review. S.B. and S.L. wrote the review and constructed the figures. E.R. reviewed and edited the manuscript, contributed references, discussions and supervised the writing. All authors have read and approved the final manuscript.

Competing interests

A patent application (Application Number GB2301443.4) covering solar reforming of plastics coupled to enzyme pre-treatment has been filed by Cambridge Enterprise with S.B. and E.R. listed as co-inventors.

Peer review information

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Table 1 | Comparison between representative photocatalytic (PC) reforming systems. Comparison of some existing PC reforming systems for waste reforming (oxidation) coupled to hydrogen evolution reaction (HER) or CO_2 reduction (CO_2R). The production rates were normalised with respect to the solar irradiation area and time, and the experiments were conducted at room temperature in aqueous medium unless otherwise stated. The light-absorber in the composite photocatalyst is underlined. Codes for products: '[R]' indicates 'reduction product', '[O]' indicates 'oxidation product', and '[OR]' indicates 'both oxidation and reduction product'. Oxidation products have not been reported for references where they are obtained as mixtures and/or not detected or quantified. Abbreviations used: r_{areal} – areal production rate; CDs – carbon dots; MSH – metal salt hydrate; PET – polyethylene terephthalate; PCL – polycaprolactone; LCC – leaf compost cutinase; HGM – hollow glass microspheres.

#	Catalyst or System	Substrate	Pre-treatment conditions	Product(s)	r_{areal} [µmol cm^{-2} h^{-1}]	Comments	Ref
*Substrate **or** waste oxidation coupled to HER*							
1	$\underline{CdS}\|CdO_x$	cellulose	1 M KOH (pH ~14)	H_2 [R]	0.004	homogeneous	96
2	$\underline{^{NCN}CN_x}\|NiP$	cellulose	0.1 KP_i (pH ~4.5)	H_2 [R]	0.22	heterogeneous	110
3	$\underline{\text{cel-CDs}}\|NiP$	cellulose	0.1 KP_i (pH ~6)	H_2 [R]	0.06	homogeneous	97
4	$\underline{TiO_2}\|Pt$-1 wt% (rutile)	cellulose	LiBr in 0.5 M H_2SO_4 (90 ºC)	H_2 [R] arabinose [O] erythrose [O] formic acid [O]	0.29 0.15 0.05 0.20	heterogeneous; MSH solutions	115
5	$\underline{CN_x}\|Ni_2P$ panel	cellulose	0.5 M KOH (pH > 12)	H_2 [R]	0.003	PC sheet	113
6	$\underline{TiO_2}\|Pt$-5 wt%	PET powders	10 M NaOH (pH > 13)	H_2 [R]	1.56	heterogeneous	103
7	$\underline{CdS}\|CdO_x$	PET bottle	10 M NaOH (pH > 13)	H_2 [R]	0.51	homogeneous	103
8	$\underline{^{NCN}CN_x}\|Ni_2P$	PET bottle	1 M KOH (pH ~14)	H_2 [R]	0.005	heterogeneous	112
9	$\underline{TiO_2}\|Pt$-1 wt%	PCL film	Dura enzyme (pH 6-8, 37 ºC)	H_2 [R] pentanal [O] formate [O] CO_2 [O]	1.13 0.20 0.02 0.22	heterogeneous	121
10	$\underline{TiO_2}\|Pt$-1 wt%	PET film	LCC enzyme (pH 6-8, 65 ºC)	H_2 [R] formate [O]	1.06 0.14	heterogeneous	121
11	$\underline{TiO_2}\|Pt$-1 wt%	PET nano-plastics	LCC enzyme (pH 6-8, 65 ºC)	H_2 [R] formate [O]	0.16 traces	heterogeneous	121
12	$\underline{TiO_2}\|Pt$-1 wt%	PET film	LCC enzyme (pH 6-8, 33 ºC)	H_2 [R] formate [O]	0.01 traces	PC sheet (integrated)	121
13	$\underline{CN_x}\|Ni_2P$ panel	PET powders	0.5 M KOH (pH > 12)	H_2 [R]	0.016	PC sheet	113
14	$HGM/\underline{CN_x}\|Pt$	PET powders	1 M KOH (pH ~14)	H_2 [R]	0.12	PC floating system; 10 reuse cycles	125

15	HGM/CN_x|Ni_2P	PET powders	1 M KOH (pH ~14)	H_2 [R]	0.02	PC floating system; 10 reuse cycles	125
			*Substrate **or** waste oxidation coupled to CO_2R*				
16	TiO_2|CotpyP	cellulose	cellulase enzyme (pH ~6.5)	CO [R] H_2 [R] arabinose [O] formate [O]	0.03 0.03 0.02 0.07	heterogeneous; semi-aqueous media	82
17	TiO_2|CotpyP	PET film	LCC enzyme (pH ~6)	CO [R] H_2 [R] formate [O]	0.01 0.05 traces	heterogeneous; semi-aqueous media	121
18	HGM/TiO_2|FDH	cellulose	cellulase enzyme (pH 6.5)	formate [OR]	0.0015	PC floating system (30 ºC)	98

Table 2 | Comparison between representative photoelectrochemical (PEC) reforming systems. Comparison of some existing PEC systems for waste reforming (oxidation) coupled to hydrogen evolution reaction (HER) or CO_2 reduction (CO_2R). The production rates were normalised with respect to the solar irradiation area and time, and the experiments were conducted at room temperature in aqueous medium unless otherwise stated. FE: Faradaic efficiency. The light absorbers in the PEC systems are underlined. Codes for products: '[R]' indicates 'reduction product', '[O]' indicates 'oxidation product', '[OR]' indicates 'both oxidation and reduction product', and '[M]' indicates 'product through a mediated process'. U_{app}: applied voltage (for a two-electrode system); E_{app}: applied potential (for a three-electrode system). Oxidation products and selectivity have not been reported for references where they are not detected or quantified. Abbreviations used: r_{areal} – areal production rate; FE – Faradaic efficiency; PVK – perovskite photovoltaic device; PET – polyethylene terephthalate; RHE – reversible hydrogen electrode; SHE – standard hydrogen electrode; PMA – phosphomolybdic acid; HMF – 5-hydroxymethylfurfural; DFF – diformylfuran; EG – ethylene glycol.

#	Catalyst or System	Substrate	Pre-treatment conditions	Product(s)	r_{areal} [μmol cm^{-2} h^{-1}]	Selectivity or FE [%]	Comments	Ref
				Substrate or waste oxidation coupled to HER				
1	Pt|PVK|$Cu_{30}Pd_{70}$ 2-compartment	cellulose	ball-milling + hydrolysis	H_2 [R] gluconate [O]	127.9 85.4	98.9 66.7	U_{app} = 0 V (1 M KOH)	149
2	Pt|PVK|$Cu_{30}Pd_{70}$ artificial leaf	cellulose	ball-milling + hydrolysis	H_2 [R] gluconate [O]	43.8 26.8	75.9 61.0	U_{app} = 0 V (1 M KOH)	149
3	Pt|PVK|$Cu_{30}Pd_{70}$ 2-compartment	PET bottle	1 M aq. KOH (pH ~14)	H_2 [R] glycolate [O]	74.8 33.9	96.7 90.6	U_{app} = 0 V (1 M KOH)	149
4	Pt|PVK|$Cu_{30}Pd_{70}$ artificial leaf	PET bottle	1 M aq. KOH (pH ~14)	H_2 [R] glycolate [O]	70.5 30.5	91.7 86.5	U_{app} = 0 V (1 M KOH)	149
5	Pt|PVK|$Cu_{30}Pd_{70}$ 2-compartment	glycerol	-	H_2 [R] glycerate [O]	112.9 44.4	- 79.0	U_{app} = 0 V (1 M KOH)	149
6	Pt-Ti-FM|PVK|CNT 2-compartment	lignin	PMA mediated[a]	H_2 [R] vanillin [M] aceto-vanillone [M]	512 - -	-	U_{app} = 0 V (0.5 M H_2SO_4)	174
7	Pt-black|Si|CNT	lignin	PMA mediated[a]	H_2 [R] vanillin [M] CO [M]	12 - -	-	E_{app} = 0.8 V vs. RHE (0.5 M H_2SO_4)	175
8	Pt|TiO_2|C@Cr-$SrTiO_3$	glucose	-	H_2 [R]	32.2	-	E_{app} = –0.3 V vs. SHE (0.5 M KOH)	169

9	Pt|Bi_2WO_6	glucose	-	H_2 [R] CO_2 [O]	3.05 -	-	E_{app} = 0.9 V vs. SHE (0.1 M Na_2SO_4/PO_4^{3-})	176
Substrate or waste oxidation coupled to CO_2R								
10	FDH|mITO||STEMPO/ DPP-CA|$mTiO_2$	HMF	-	formate [R] DFF [O]	0.16 0.19	~100 86	U_{app} = 0 V (0.1 M $Na_2B_4O_7$)	172
11	NiOOH/Fe_2O_3 ||Bi/GaN/Si	Raw biomass	Thermal (>100 ºC) + acid treatment	formate [OR]	23.3	>90	U_{app} = 0 V ($KHCO_3$|KOH)[b]	177
12	CoP_L|PVK||$Cu_{27}Pd_{73}$	PET bottle	1 M KOH (pH ~14)	CO [R] H_2 [R] glycolate [O]	26.3 4.6 12.3	~95.6 ~16.9 97.5	U_{app} = 0 V ($KHCO_3$|KOH)[b]	83
13	$Cu_{91}In_9$|PVK||$Cu_{27}Pd_{73}$	PET bottle	1 M KOH (pH ~14)	CO [R] H_2 [R] glycolate [O]	21.3 24.0 21.0	~42.8 ~48.6 95.8	U_{app} = 0 V ($KHCO_3$|KOH)[b]	83
14	FDH|PVK||$Cu_{27}Pd_{73}$	PET bottle	1 M KOH (pH ~14)	formate [R] glycolate [O]	12.1 5.7	~96.4 96.1	U_{app} = 0 V (MOPS|KOH)[b]	83
15	$CoPcNH_2$|PVK|| $Cu_{26}Pd_{74}$	EG (ideally from PET)	0.5 M KOH	CO [R] H_2 [R] glycolate [O]	4.68 18.1 10.2	21.0 81.1 89.4	U_{app} = 0 V (TEA/H_2O|NaOH/EG)[b] flue-gas (15% CO_2)[c]	84
16	$CoPcNH_2$|PVK|| $Cu_{26}Pd_{74}$	EG (ideally from PET)	0.6 M NaOH/ MeCN	CO [R] H_2 [R] glycolate [O]	0.02 0.51 0.56	2.3 60.8 85.7	U_{app} = 0 V (NaOH/EG|NaOH/EG)[b] (DAC, 440 ppm CO_2)[d]	84

[a] PMA-mediated process indicates that the phosphomolybdic acid (PMA) pre-reduced by biomass is used at the anode.

[b] (A|B) indicates 'A' as the catholyte and 'B' as the anolyte.

[c] PEC system where CO_2 from flue-gas is captured (TEA/H_2O as capturing agent or medium) and converted at the photocathode.

[d] PEC system where CO_2 from ambient air is captured (NaOH/EG as the capturing agent or medium) and converted at the photocathode.

Fig. 1 | Overview of current and future economic models. a, Schematic of current 'linear' chemicals industry where fossil fuels provide energy and feedstocks to produce goods that are primarily discarded at end-of-life. **b,** Schematic of net-zero circular economy scenario in 2050 using solar reforming to drive chemicals production from biomass, atmospheric CO_2, and recycled waste. Colours represent different categories of streams; green: recycled mass, brown: waste mass, black: fossil fuel mass, white: processes, red: energy.

Fig. 2 | Overview of solar reforming categories and deployment architectures. Top: Categorisation of solar reforming depending on the utilisation of incoming sunlight spectrum. Percentages indicate the fraction of solar irradiance found in each spectral component. **Bottom:** Solar reforming (primarily solar catalytic reforming which predominantly utilises visible solar spectrum) can be deployed in three architectures: photocatalytic (PC), photoelectrochemical (PEC), and photovoltaic-electrochemical (PV-EC). PC deployment can be improved through immobilisation strategies to improve re-use while PEC's deployment can be made more flexible through integrated device designs. 'products' refers to CO_2 reduction (CO_2R) products currently demonstrated in the literature, including CO, primary alcohols, and formate.

Fig. 3 | Overview of solar-driven waste reforming process. Schematic illustration outlining pre-treatment approaches and sample monomers useful for waste reforming in solar-powered recycling plant. The pre-treatment step depends on waste composition, whereas liquid effluents (with or without separation) and gaseous CO_2 (from flue-gas, air) may be directly used in solar reforming systems to produce fuels and chemicals. The conversion efficiencies depend on the nature of the substrate and vary significantly in each case, and often maximum conversion is achieved through the combination of two or more pre-treatment approaches[17,22]. Abbreviations used: PET – polyethylene terephthalate; MHET – monohydroxyethyl terephthalate; alk – alkaline; DAC – direct air capture.

Fig. 4 | Thermodynamics of solar reforming and artificial photosynthesis. Schematic showing the interconnection and standard redox potentials of both processes with the balanced equations and Gibbs' free energy changes for individual steps: Overall water splitting: $2H_2O \rightarrow 2H_2 + O_2$ ($\Delta G_{OWS} = 237$ kJ mol^{-1}); natural photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ ($\Delta G_{NP} = 2872$ kJ mol^{-1}); hydrogen combustion: $2H_2 + O_2 \rightarrow 2H_2O$ ($\Delta G_{use} = -237$ kJ mol^{-1}); solar reforming with biomass model substrate (glucose): $C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$ ($\Delta G_{SR} = -35$ kJ mol^{-1}). Solar-to-fuel efficiency (η_{STF}) is given by eq. (1) where r is the rate of product formation (mol s^{-1}), P is the light intensity flux (W m^{-2}) and A is area (m^2). In the sample efficiency calculations, values were arbitrarily selected: $r = 0.5$ mmol s^{-1}, $P = 1$ kW m^{-2} and $A = 1$ m^2. Abbreviations used: ΔG_{OWS} – Gibbs' free energy change for overall water splitting; ΔG_{OWS} – Gibbs' free energy change for overall water splitting; ΔG_{SR} – Gibbs' free energy change for solar reforming; ΔG_{use} – Gibbs' free energy change during utilisation of fuel produced; E^o_{OWS} – standard redox potential for overall water splitting; E^o_{SR} – standard redox potential for solar reforming; E^o_{NP} – standard redox potential for natural photosynthesis; E^o_{use} – standard redox potential for H_2 fuel utilisation.

Fig. 5 | Overview of photocatalytic (PC) reforming. a, Schematic illustration of PC reforming on a photocatalyst. VB – valence band; CB – conduction band. **b,** Detailed depiction of individual steps during PC reforming on a semiconductor photocatalyst: (i) Light absorption resulting in (ii) exciton (electron-hole pair; e^- indicates an electron and h^+ indicates a hole) generation, (iii) charge separation and transfer to the photocatalyst surface, (iv) charge recombination, (v) extraction and utilisation of excited electrons for reduction by a co-catalyst, (vi$_a$) utilisation of holes for direct oxidation of substrate adsorbed on the surface of the photocatalyst, (vi$_b$) utilisation of holes for $OH^•$ radical generation under aqueous conditions, (vii) substrate oxidation in solution via $OH^•$, (viii) desorption of oxidised substrate (product) from the photocatalyst surface, (ix) photocatalyst surface poisoning by oxidation intermediates. 'S' indicates substrate; 'S^+' indicates oxidised substrate; 'S_{ads}' indicates adsorbed substrate. CO_2 reduction (CO_2R) products may include CO, syngas, formate, alcohols or hydrocarbons. Adapted from ref. [106] **c,** Approaches for improving the recyclability and recovery photocatalysts during PC reforming. **d,** Photographs of different types of PC reforming systems and configurations. The scale bars correspond to 1 cm.

Fig. 6 | Photoelectrochemical (PEC) and photovoltaic-electrochemical (PV-EC) reforming systems. Simplified schematic of (**a**) waste pre-treatment step(s) and (**b**) the different types of redox catalysts (molecular, metallic or biological) that can be integrated into the PEC or PV-EC architectures ('*n*' is a positive integer indicating number of electrons involved in a redox process). **c, d,** Conventional two-compartment PEC arrangements with single light absorber either as a (**c**) photocathode or (**d**) photoanode, sandwiched between charge transport layers and connected to a 'dark' counter electrode. **e,** Standalone, monolithic 'artificial leaf' for PEC reforming. **f,** Typical architecture of a PV-EC reforming system (PV module indicates photovoltaic module). CO_2 reduction

(CO_2R) products may include CO, syngas, formate, alcohols or hydrocarbons. Abbreviations used: FTO – fluorine-doped tin oxide; HTL – hole-transporting layer; ETL – electron-transporting layer. Note that ETL and HTL layers are often included in photovoltaic devices to improve charge separation, but are not always required with photocatalysts (deposited to make photoelectrodes) that have innately higher recombination times (for example, TiO_2 or CN_x)[158].

Short Summary

This review introduces solar reforming as an emerging technology to produce sustainable fuels and chemicals from diverse waste feedstocks using sunlight. We discuss the concept, key metrics and propose directions to realise solar-powered refineries for a future circular economy.