

Review

A carbon neutral chemical industry powered by the sun

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Abstract

The decarbonisation of the chemical industry requires a transformation of the sources of energy, raw materials, and structure of the sector. The production of chemicals by converting fossil fuels is a pillar of the modern economy, consuming 10% of global energy demand and releasing 7% of global CO₂ emissions. Being the most abundant source of energy available to humankind, solar energy can provide solutions across the different needs identified to deploy a low-carbon and sustainable industry. However, its transformation into functional energy and chemical feedstocks presents multiple challenges at the technical, economic, environmental, and social levels. While solar energy is being largely deployed, its incorporation within the chemical sector requires a guarantee of supply at feasible costs. Analysing alternative feedstocks, even mature processes struggle to reach competitive prices, a situation that worsens as technologies at early development stage are considered. Despite these, and other challenges, the use of solar energy is a general trend that is widely accepted within the chemical and other industries, with increasing research efforts aiming to present solutions to guarantee its sustainable implementation. The penetration of these technologies into the existing structure of the sector calls for a process systems engineering thinking, which combined with life cycle assessment, can shed light into the sustainable deployment of solar-based processes. On this basis, we present the status of solar technologies and their potential contribution to achieve a sustainable industry. This perspective thus presents an analysis of solar technologies that can support the transition of the sector in the short, middle, and long term, and the challenges inherent to their implementation. While the transition of the chemical industry from fossil fuels to solar technologies seems promising and shows significant abatement of CO₂ emissions, it is expected to occur at the expense of higher production costs and unintended environmental burden shifting. Therefore, the application of sustainable process systems thinking at a multi-scale level will be key to identify energy-efficient and highly-integrated systems deployed within local and regional contexts. These tools will ultimately assist the decision-making process to guide a global environmental policy framework that promotes sustainable development and ensures competitiveness of the sector across multiple regions.

Abbreviations

AEC	Alkaline electrolysis cells
ATR	Autothermal reforming
BECCS	Bioenergy with carbon capture and storage
CAMD	Computer aided molecular design
CCS	Carbon capture and storage
CCUS	Carbon capture, utilisation and storage
Cefic	European Chemical Industry Council
CO ₂ eq	Carbon dioxide equivalent

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IEA	International Energy Agency
ISO	International Organisation Standardization
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
MTO	Methanol to olefins
PEM	Proton exchange membrane electrolyser
PSE	Process systems engineering
PtG	Power to gas
PtL	Power to liquids
SMR	Steam methane reforming
SOEC	Solid oxide electrolysis cells
Solar CSP	Solar concentrated solar power
Solar PV	Solar photovoltaics

1 Introduction

The chemical industry relies on fossil fuels as a source of energy and feedstocks, releasing significant amounts of CO₂ and other pollutants into the environment. The increasing desire to develop a sustainable society places a strong motivation to decarbonise the chemical sector and achieve the climate goals proposed in the Paris agreement and recently established net-zero targets [1, 2]. In this context, different strategies have been identified to transition away from fossil fuels and reduce the carbon footprint of the chemical sector [3, 4]. Some examples include the capture of CO₂ and eventual shift toward renewable carbon feedstocks, the integration of circular economy practices, electrification of the industry powered by renewable sources, and reduced energy consumption via technological improvements.

Being the most abundant source of energy available to humankind, solar energy can play a prominent role among these strategies to attain a decarbonised chemical sector. The impressive supply of solar energy is complemented by its versatility. Sunlight can be converted into electricity by exciting electrons in a solar cell, generate fuels or chemicals via natural or artificial photosynthesis or produce heat with concentrated or unconcentrated sunlight [5, 6]. However, solar energy is diffuse and intermittent, requiring techniques for its capture, conversion, long-term storage, and long-range distribution. In addition to the technical challenges posed for the conversion of solar energy and feedstocks, there are those related to social, economic, and environmental criteria beyond CO₂ emissions. At present, the chemical industry is a highly integrated and complex entity that promotes economic growth and brings solutions across multiple sectors, showing also limited opportunities for innovation given the high costs that it might induce [3, 7]. In addition, the sector is also responsible for the release of CO₂ emissions and other pollutants into air, water, and soil, as well as the consumption of energy and resources. Therefore, any transition toward sustainable development should present a full and holistic assessment of the alternatives proposed to attain this goal.

In this context, we here present a perspective about the role of solar energy and feedstocks within the chemical industry to produce chemicals with a reduced carbon footprint. Based on a process systems engineering (PSE) thinking, we address how multi-scale process modelling and optimisation, in combination with life cycle assessment (LCA), can support the decision making to attain a solar-based sustainable industry. We start by presenting a current picture of the chemicals sector, where the need for a transition from fossil fuels as source of energy and feedstocks is highlighted. We next discuss some of the attributes that make solar energy an attractive alternative for the sector. Here, we analyse the progress made in the generation of solar energy, including electricity, heat, and their storage. While the basic concepts related to each technology are addressed, the discussion of advances in material science is out of the scope of this work. We then analyse solar feedstocks and their transformation, addressing natural and artificial photosynthesis along with the implications pertaining to their large-scale implementation. Next, we discuss how solar technologies can contribute to a carbon neutral industry in the short, medium, and long term. In this section, we first present how PSE and LCA can support decision making to attain sustainable development from early design stages to the design of supply chains at regional levels. On this basis, we finally analyse their role to deploy solar technologies at a sustainable pace. While the

focus of this perspective is placed on solar energy, most of the discussion can be expanded to other renewable or clean energy sources, such as wind or nuclear.

2 Current status of the chemical industry

The chemical sector is a complex network of many diverse and interacting subsectors covering multiple feedstocks, processes, and products that are moved around on national and international scales. Through the production of base, speciality, and final-end products, chemicals consume around 10% of global energy demand and release 7% of global CO₂ emissions. With an investment of over a multitrillion-dollar infrastructure over the last century, the products conceived by the sector provide solutions for the needs of society and are an important part of the economy. In 2017, the sector directly employed 15 million people and generated global annual sales for \$3920 billion, representing 7% of the world's gross domestic product. If we consider its supply chain and payroll-induced impacts, this value increases to an estimate of \$5700 billion and 120 million jobs supported. The growth attained by the sector is expected to continue in the coming decades with sales reaching \$7450 billion by 2030 [8]. As the transition toward carbon neutrality is pursued, it is therefore important to ensure that these jobs and economic activity are conserved and grown as part of the transition to a sustainable economy.

The chemical industry is sustained by fossil fuels (Fig. 1), where oil and gas make up around 90% of the raw materials. The steam cracker is at the heart of organic compounds, generating high value chemical building blocks (e.g. ethylene, propylene, butadiene, and aromatics) from oil or natural gas. Inorganic compounds include subdivisions such as heavy inorganics (e.g. chlor-alkalis, sulfuric acid, sulfates) and fertilisers, which find hydrogen from natural gas as one of their main feedstocks. At present, the Middle East is the primary global supplier of low-cost key petrochemicals. The shale gas revolution provided a new boost to the sector in the US, which produces now around 40% of low-cost ethane-based chemicals. China and Europe share a quarter of naphtha-based high-value chemicals, with a Chinese coal-based industry flourishing through technological improvements.

In 2015, the sector consumed 43 EJ/y (Fig. 1), from which 25 EJ/y came from oil and natural gas used as feedstock, while the rest were attributed to energy supply [3]. Being fossil fuels the source of energy and carbon for the industry, their extraction, use, and final disposal, result in an increased concentration of CO₂ in the atmosphere. That is, the emissions from the sector come across its entire supply chain and throughout the lifecycle of its products. As a result, the chemical sector released roughly 0.3 Gt CO₂eq during the extraction of raw materials, 2.1 Gt CO₂eq during the manufacturing process, and 0.9 Gt CO₂eq during the disposal phase. Within the manufacturing stage, one third were released during the processing of feedstocks, other third from fuels to produce heat, and the remaining third came from electricity (machine drive) and other utilities [3].

Figure 2 shows the most energy intensive products of the sector in 2018, which are equally the ones with the largest production volumes and contribution toward CO₂ emissions [9]. Ammonia is the chemical with the largest volume and is produced via the Haber–Bosch process using coal gasification or steam reforming of natural gas as hydrogen source. The process release ~550 Mt CO₂eq, from which two-thirds are used to produce urea, a fertiliser based on CO₂ and ammonia. The CO₂ used in the production of urea is ultimately released after the consumption of the fertiliser. Like

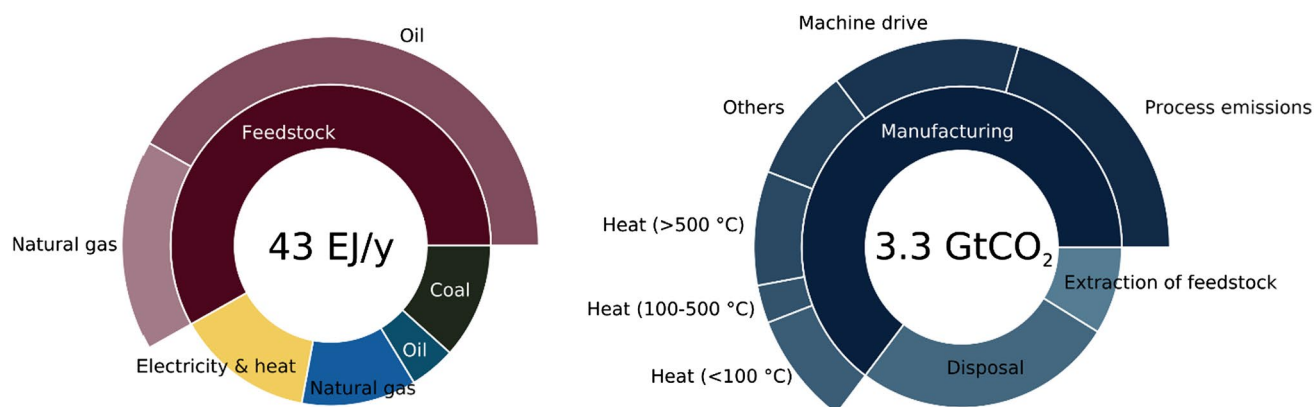
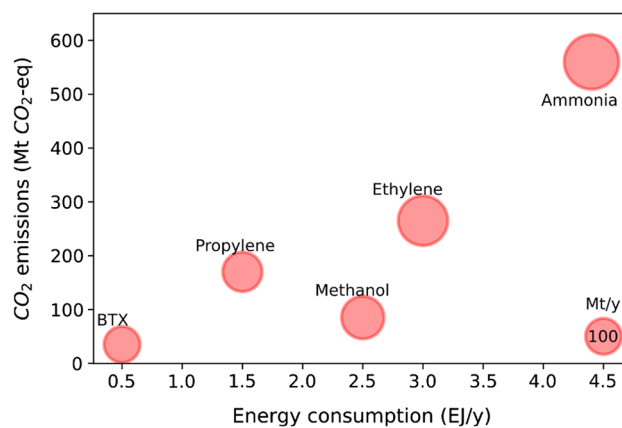


Fig. 1 Energy consumption and emissions released by the chemical industry in 2015. Adapted from Pee et al. [3]

Fig. 2 Energy consumption and emissions released by the chemicals with the largest production volume in 2018. Adapted from IEA [9]



ammonia, methanol is also produced from coal and natural gas and is responsible for the release of ~90 Mt CO₂eq. In this process, syngas is produced from the corresponding fossil-based feedstock and then converted into methanol via the water–gas shift reaction. Methanol finds a wide range of applications, either as chemical building block (producing acetic acid, formaldehyde, or olefins) or used directly as fuel or as an additive via methyl-tert-butyl ether (MTBE) or dimethyl ether (DME). Finally, the ~475 Mt CO₂eq released by ethylene, propylene and aromatics (BTXs) are the result of fuel combustion required in the steam cracking processes, which operate at temperatures of 650–900 °C [10]. These are platform chemicals used in the production of a wide range of organic chemicals and polymers.

Whilst the sector is directly responsible for the release of ~7% of global CO₂ emissions, it also plays a significant role for the decarbonisation of other sectors. A study carried out in 2005 showed that the solutions brought by the sector to other industries (e.g. insulation materials, CFL lightning, PVC windows, synthetic textiles, etc.) allowed savings of 2.1 to 2.6 kg CO₂eq per kg of carbon emitted [11], and the CO₂ abated could reach 4.0 kg CO₂eq by 2030 [12]. In addition, the chemical industry has always been in constant improvement and searches for new ways to enhance processes and energy efficiency, although the primary motivation has been the reduction in production costs. An example of this is the UK's chemical industry, which has reduced its energy consumption by 40% in the last 30 years despite an increase of over 40% in industrial output in value-added terms [12, 13]. This reduction covers multiple underlying causes, like end-use efficiency, structural changes in industry (moving away of heavy industries, more energy-efficient technologies, and economies of scale), and fuel switching [14]. Despite these continuous improvements, a substantial transformation is still required to reach the final goal of a carbon neutral industry and sustainable development. According to the reference scenario depicted by the International Energy Agency (IEA) in 2017 [15], the production of chemicals is expected to increase by 50% in 2050, implying an increase in energy consumption and sectoral CO₂ emissions if no measures are implemented.

3 Solar technologies and their potential to decarbonise the chemical industry

The decarbonisation of the chemical industry involves the reduction of CO₂ emissions across its supply chain by closing and abandoning the current paradigm of relying exclusively on fossil carbon. Different roadmaps address the challenges faced to decarbonise the sector [3, 4, 9, 15, 16]. Measures include demand-side actions, energy efficiency, electrification of heat, hydrogen and biomass as fuel or feedstock, carbon capture, utilisation and storage (CCS/CCUS), and other strategies and innovations, such as an increased plastic recycling capacity, or (photo) electrocatalytic processes. As observed from Fig. 1 and these strategies, at the core of this transformation lies the need for renewable energy and feedstocks.

Among the different renewable sources, solar energy is the most abundant source of energy available to humankind. Solar energy equivalent to the total world fossil fuel energy reserves falls on the earth in fewer than 14 days, and 1 h of energy from sunlight ($4.3 \cdot 10^{20}$ J) is almost enough to satisfy the global demand of energy in the planet ($4.6 \cdot 10^{20}$ J) [17]. The impressive supply of solar energy is complemented by its versatility (Fig. 3). Sunlight can be converted into electricity by exciting electrons in a solar cell, generate fuels or chemicals via natural or artificial photosynthesis or produce heat with concentrated or unconcentrated sunlight. However, the regions where this resource is available for harvesting do not coincide with centres of great energy demand and solar energy is also diffuse and intermittent, requiring techniques

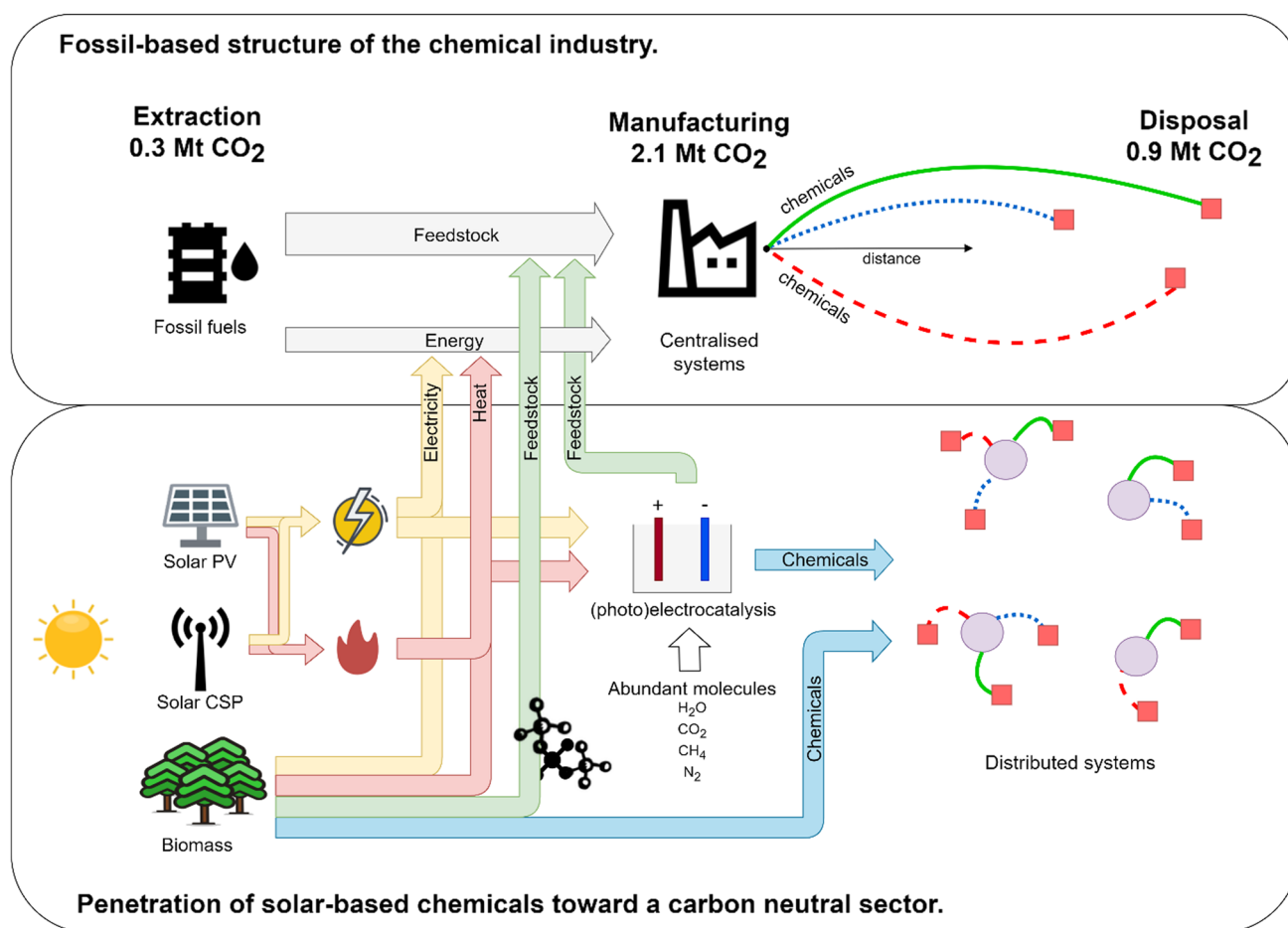


Fig. 3 Areas for penetration of solar technologies into the current structure of the chemical sector

for its capture, conversion, long-term storage, and long-range distribution. As a result, only 3% of electricity consumption is provided by solar energy [18], 0.02% of industrial heat demand is satisfied by solar thermal [19], and roughly one-tenth of global primary energy is provided by biomass [20, 21].

In consequence, if solar energy is to become a practical alternative to fossil fuels within the chemical sector, we must find efficient ways to convert photons into electricity, heat, fuels, and feedstocks. Here, different schemes have envisioned the use of solar energy as a source of energy and raw materials within the chemical sector [5, 6, 22–24]. However, despite the progress being made, still several key opportunities, as well as knowledge and capability gaps, remain to be developed. In this section, we present an overview of the progress attained by solar technologies and their potential applications within the chemical sector.

3.1 Solar energy and storage

3.1.1 Solar electricity

In this process, cells capture photons by exciting electrons across the bandgap of a semiconductor, which creates electron–hole pairs that are then charge separated. The best commercial cells are silicon photovoltaics (PV) (single-junction), reaching commercial efficiencies around 22%, with a maximum of 26.7% reported at lab scale, relative to the Shockley–Queisser limit of 31% [23]. This theoretical limit, however, can be increased up to 40% for unfocused sunlight using multiple bandgaps in a single heterostructure, also known as multi-junction [25]. Despite their higher efficiency, multi-junction cells are much more difficult to manufacture than single-junction cells given the current/voltage matching criterion required [26]. Solar PV covers more than 90% of the market with a lifetime superior to 25 years and installed capacity doubling every 2 to 3 years. In 2019, solar PV generation increased by 22%, bringing the world's capacity to 720

TWh, and it is expected to provide 3000 TWh per annum by 2030 [18]. The recent drop in cost of Si-based solar panels, caused by an increased production in China, has made solar electricity costs competitive compared to traditional routes in some markets, reaching values of \$60/MWh_e [27–29]. In recent developments, perovskite panels are proposed as a cheaper, more efficient alternative, which also relies on abundant materials. These systems have reached an efficiency of 24.2% at lab scale, although challenges remain to scale-up that performance and prove their longevity and efficiency on field [30]. Companies like Saule have recently reached the market while others like Sekisui Chemical expect to reach it in 2021, reaching another milestone for this technology.

Solar PV cells are not the most efficient way to convert sunlight into electricity. By concentrating sunlight, the Shockley–Queisser limit can be exceeded up to 41% for a single-junction cell, 43% for a two-junctions system, and up to 66% for an infinite-junctions system [23]. In concentrated solar power (CSP) installations, parabolic mirrors concentrate sunlight onto pipes containing a high boiling liquid, and the heat is then used to raise steam, which operates coupled to a thermal cycle. Conventional induction generators powered by steam engines driven by solar heat reach efficiencies of 20% on average and 30% for the best systems. These values are still way below their theoretical limit and ways to improve them include large-scale plants operating at high temperatures (> 1500 °C) or the use of thermoelectric materials which can produce electricity from thermal gradients without the need for moving parts. The most promising materials are nanostructured composites. The cost of CSP plants has decreased by 47% from 2010 to 2020 reaching a minimum cost of \$110/MWh, and there are currently more than 100 CSP projects in the world [19, 29, 31].

3.1.2 Solar heat

In addition to the direct use of renewable electricity, power-to-heat is expected to be the first type of electrification that chemical companies will implement. In a thorough review of solar technologies applied to industrial applications, Schoeneberger et al. [32] pointed that roughly 50% of industrial heat used by the most energy-intensive industries in the US occurs at temperatures of 300 °C or less. As reported by the authors, this presents a great opportunity for solar-based systems, which already operate at temperatures from 60 to 250 °C. Non-tracking collectors are the most common systems to provide heating up to 80 °C. Technologies available include flat plate collectors, evacuated tube collectors, and compound parabolic collectors. In a different approach, solar CSP can provide the heat of reaction in chemical processes either by the heating of the reactor or reactants, avoiding the use of fossil fuels to provide the energy required. Applications within the sector include steam methane reforming, gasification of coal, steam electrolysis, or conversion of CO₂ into carbon monoxide and oxygen [33]. There are different CSP technologies available. Among them, parabolic troughs are the most common technology deployed generating temperatures around 400 °C. Power towers represent another option, reaching temperatures of 650 °C or more. In this system, mirrors are arranged in a circular shape and focus sunlight to the towers where a molten salt (or heating fluid) absorbs the sunlight heat and increases the temperature. The molten salt flows to a reservoir and store the heat energy, which can then be used in the corresponding processes [23, 34]. This application presents some challenges, such as maintaining constant temperatures along the reactor, intermittent production, or safety and materials issues [33].

Solar PV can also be used directly to provide heating to the sector. Some technologies available include resistance and induction heating, heat pumps, microwave processing, electric boilers, and industrial furnaces [3, 32, 35]. In an innovative approach, Wismann et al. [36] showed that gas-fired steam reforming reactors can be substituted by electrical ones, reducing the emissions of the process by a quarter. In their study, the reactor wall was coated with a catalytic layer that worked as an electric resistance, which generated heat when an electric current was applied. The reaction was carried out close to thermal equilibrium and improved selectivity and yield, pointing to potential ways to electrify the chemical industry. Other examples include the use of 3D-printed materials suitable for electric swing adsorption processes applied for CO₂ capture [37], and the use of microwave heating to improve selectivity in solid–gas heterogeneous catalytic processes [38].

3.1.3 Energy storage

A technical challenge to spread the use of solar energy is that of energy storage, which is still expensive, and most schemes seek to minimise its direct implementation. Some of the alternatives available include electrochemical storage (batteries), pumped hydropower, or thermal storage [39, 40]. Schmidt et al. [41] analysed the future costs of electricity storage based on experience rates and concluded that storage capital costs are \$340/kWh for installed stationary systems and \$175/kWh for battery packs after 1 TWh of installed capacity is reached. While systems like pumped hydro have reached this level, others like lithium-ion (utility) are still far from it, with current costs of \$500/kWh. This would represent

not only additional costs to the manufacture of chemicals and more complex systems but also more energy demanding and polluting processes. For instance, McManus [42] reported emissions of 17–27 kg CO₂eq/MJ in the manufacture of lithium-ion batteries, also pointing to potential impacts to human health as well as social effects during the mining of lithium. In terms of thermal energy storage, systems available include sensible heat storage, latent heat storage, and thermochemical storage. Sensible heat storage relies on storing heat as internal energy that is released through changes of temperature. Water is the most common technology given its cost, simplicity, and high specific heat [32]. Latent heat storage relies on the phase change of materials at constant temperature, with fluids operating between 100 and 900 °C [32]. Finally, the ability to store heat into chemical bonds provides an alternative to overcome the intermittency of solar energy at potentially lower prices. In this context, different energy vectors have been considered, such as biomass, hydrogen, ammonia, or methanol [43]. In the case of hydrogen, for instance, storage in salt caverns has an average cost of \$7/kWh while bulk compressed hydrogen can reach costs around \$40/kWh [44]. The challenge, however, is to facilitate networks for their distribution. The transformation of electricity into chemical bonds is of particular interest to the chemical sector, as these materials work not only as energy sources but also as feedstocks.

The large-scale implementation of solar electricity in the chemical sector still seems distant as most of this deployment is connected to the grid to decarbonise the energy sector. In addition, some of the technologies discussed are still at early development stage and their industrial implementation is still to be demonstrated. Yet, cases like the Italian oil and gas company Eni already display the implementation of solar PV within the industry. In their announcement, the company mentioned the completion of a 31 MW solar PV plant on one of its industry sites in Sardinia. This plant is expected to generate 50 GWh of electricity per year, having around 70% of its output powering operations of Versalis, one of Eni's chemical subsidiaries [45].

While there are technologies available for the use of solar electricity and heat within the sector, one of the primary challenges relate to guarantee the supply at feasible costs [40, 46]. For instance, while electric boilers and industrial furnaces are expected to have similar capital costs and efficiencies to conventional options, their deployment will only be economical when electricity costs are the same as fossil fuel alternatives. In 2017, the average weighted global levelised cost of solar PV was \$90/MWh, with values ranging from \$60–310/MWh and capacity factors from 0.13 to 0.23. That of solar CSP in 2016 reached \$270/MWh with a range from \$140–350/MWh and an average capacity factor of 0.33. These costs are still far of presenting cost-competitive options for the sector. For instance, Pee et al. [3] reported that electricity costs of ~\$25/MWh would make electrification of heat in ethylene production more cost-competitive than applying CCS to conventional processes.

In terms of CO₂ emissions, solar PV releases from 0.07 to 0.10 kg CO₂eq/kWh for single junction and around 0.03 kg CO₂eq/kWh for multi-junction. A recent study on perovskites panels reported emissions around 0.01 kg CO₂eq/kWh [47] while solar CSP ranges from 0.02 to 0.05 kg CO₂eq/kWh. These options represent significant savings compared to coal or natural power plants, which release 1.01 and 0.43 kg CO₂eq/kWh with potential reductions by 2050 of 0.11 and 0.08 kg CO₂eq/kWh when coupled with CCS, respectively [48]. To analyse the impact of solar electricity to decarbonise the chemical sector, let us consider the 6 EJ/y of electricity and low temperature heat consumed in 2015 (Fig. 1). If we assume a carbon intensity of 0.30 kg CO₂eq/kWh (representative of the average European electricity mix), this will result in approximately 500 Mt CO₂eq. A shift to solar PV with a carbon intensity of 0.085 kg CO₂eq/kWh would incur 140 Mt CO₂eq, representing an annual reduction in CO₂ emissions of 72%. In addition to CO₂ emissions, the use of solar PV could bring benefits in other environmental categories, such as eutrophication, particulate matter formation, and ecotoxicity. However, this will come at the expense of larger land occupation and consumption of bulk materials, such as iron, copper, aluminium, and cement [49]. Among renewables, such as wind or nuclear, solar PV still represents the most polluting technology. The reason being the energy-intensive processes required for their manufacture, which are still dependent on fossil fuels. However, as the global energy mix decarbonises toward 2050, emissions from both solar PV and CSP are expected to decrease up to 0.01–0.02 kg CO₂eq/kWh, reaching similar levels as wind or nuclear [48]. Under this scenario, the sector would release 16 Mt CO₂eq for the same 6 EJ/y if a carbon intensity of 0.01 kg CO₂eq/kWh is achieved.

3.2 Solar feedstocks: biomass

Biomass has been used for centuries to store solar energy into chemical bonds. An estimated of 100 TW of solar energy go into photosynthesis, where nature converts sunlight into biomass at a yearly average efficiency of 0.3% [17]. One use of biomass is its conversion into bioenergy, which used together with flexible technologies within the sector, is often associated with low-carbon and even negative emissions when coupled with CCS facilities (BECCS). At present, the main

uses of bioenergy are power and fuels, with carbon efficiencies from 17–38% and 45–50%, respectively [50]. Global production of biofuels reached 154 billion litres in 2018 and is expected to increase to 193 billion by 2024 [21]. Bio-electricity, on the other hand, reached a generation of 589 TWh in the same year with a forecast of 900 TWh by 2024 [20].

Biomass can also be used as feedstock to produce chemicals with a minimum or negative carbon footprint. Its use represents the direct consumption of naturally stored CO₂, resulting in an attractive option for processes difficult to decarbonise throughout its entire lifecycle, like ethylene/plastics and ammonia/fertilisers. Feedstocks include starch and sugar (first generation), lignocellulose (second generation), and algae (third generation). First generation feedstocks compete with their use as food, influencing their cost and supply. In this context, waste and lignocellulosic sources represent an attractive low-cost, abundant alternative, which is acknowledged as the next source of biomass to produce chemicals. In the case of algae, conversion technologies are still required with a substantial cost reduction to make them competitive.

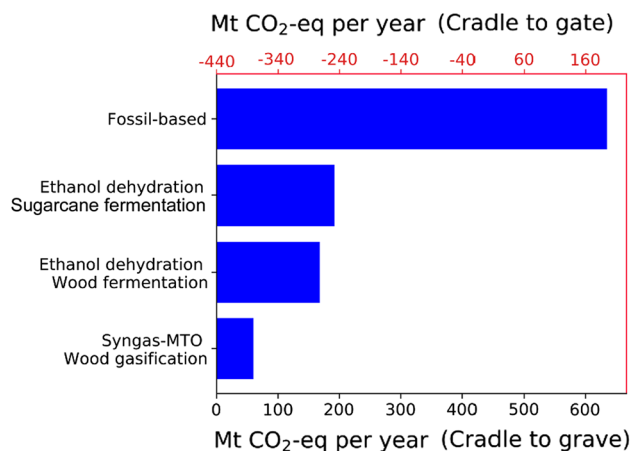
Biomass is a heterogeneous mixture of compounds that include cellulose, hemicellulose, starch, chitin, and lignin, itself a sophisticated assembly of complex compounds, such as coniferal alcohols. Depending on the source of biomass, other components can also be present, such as fats, waxes, proteins, among others. Given the complexity of this mixture, appropriate conversion methods are required to exploit biomass potential. Gallezot [51] pointed that biomass structure should be the first factor to define the use of the biomass instead of trying to produce platform chemicals that follow current practices. Carbohydrates (C5 and C6 sugars) are the most common feedstock to produce commodity and specialty chemicals. The three most well know alternatives for biomass conversion are direct fermentation of starch/sugar, hydrolysis of lignocellulosic biomass, and lignocellulosic biomass pyrolysis/gasification [13]. The result of these processes are platform molecules in the range C1 to C6, including CO, ethanol, glycerol, lactic, succinic, and levulinic acids, or sorbitol [52]. These molecules can then be transformed into a broad range of chemicals [53]. In addition, biomass could also be used in the production of ammonia either by pyrolysis of dry biomass to produce hydrogen and CO or by gasification of wet biomass to produce methane and CO₂ [3, 54].

In terms of production costs, low-cost feedstocks (e.g. biomass residues) present competitive prices against their fossil counterparts, which could be further reduced with technological improvements. For instance, Fiorentino et al. [52] showed that bio-ethylene is 30% more expensive than its fossil counterpart, polylactic acid is just slightly more expensive, and starch polymers are 60% more expensive than low-density polyethylene. When expensive feedstocks (e.g. dedicated crops) are used, bio-based materials are significantly more expensive than fossil-based ones (above three-fold), situation that worsens as chemicals at low production levels or at R&D stage are considered. Approximately 400 biorefineries were operating worldwide in 2010. Most of them refer to conventional biorefineries, which are already mature technologies and base their production on first generation biomass as feedstock, producing biofuels, such as biodiesel or bioethanol. Conversely, advanced biorefineries are related to the use of more sustainable biomass, such as lignocellulose. The problem, however, is that most of the routes to produce fuels and chemicals are still in the R&D, pilot or demonstration scale. In addition, those operating at industrial scale face difficulties in competing with conventional facilities.

Multiple studies have already shown the viability to produce chemicals from biomass conversion with reduced CO₂ emissions [55–64]. In a biorefinery concept based on switchgrass hydrolysis, Cherubini and Jungmeier [60] showed that CO₂ emissions from cradle-to-gate could be reduced by 79% for a plant producing the same products as a petroleum-based system (fuels, heat and electricity). However, such savings are highly dependent on the type of biomass, location, technology applied, among other factors. To exemplify this, let us consider the case of ethylene production, which has an average carbon footprint of 4.5 kg CO₂eq/kg ethylene. This value corresponds to naphtha steam cracking in Europe using a cradle-to-grave analysis under economic allocation and incineration as disposal route. At present, the most popular route to produce ethylene from biomass is through ethanol dehydration, where ethanol is produced via sugarcane fermentation. This process is commercially available with several companies already in operation, such as BP, Axens, Chematur or Braskem, for a combined capacity of 255,000–800,000 t/y [61]. Liptow et al. [62] analysed this production route within the Swedish context, and determined that 1.6 kg CO₂eq/kg ethylene were released. If sugarcane was switched to wood, this same route would release 1.4 kg CO₂eq/kg ethylene. These routes present reductions of CO₂ emissions by 64 and 68% compared to the naphtha route, respectively. A different process for ethylene production is biomass gasification, which is considered as the preferred route for the advanced biorefinery concept [63]. One option for this process involves the production of syngas that is then transformed into olefins via the methanol-to-olefins (MTO) process [59, 64]. This process results in the production of ethylene and propylene at a typical ratio from 1.2 to 1.5, along with some C4 compounds. Applying the same cradle-to-grave approach and economic allocation, the MTO route would result in 0.5 kg CO₂eq/kg ethylene using wood as raw material, resulting in a reduction of CO₂ emissions by 88% [64].

From the previous example, we can observe the variety of results depending on the biomass, technology, and assumptions of the analysis. To reflect the impact of these routes in the current market of the chemical industry, Fig. 4 shows the

Fig. 4 CO₂ emissions for the production of 140 Mt of ethylene per year. Emissions from cradle-to-grave reported in black axis (bottom) and emissions from cradle-to-gate reported in red axis (top). In the cradle-to-grave approach, it is assumed that ethylene is combusted after use releasing 3.1 kg CO₂/kg ethylene



CO₂ emissions from cradle-to-grave of the alternatives described. The emissions reported here consider that ethylene is combusted after use, releasing 3.1 kg CO₂/kg ethylene. This assumption avoids the need to account for CO₂ credits during biomass cultivation. As observed, 400 to 560 Mt CO₂eq could be reduced depending on the biomass route selected. These emissions in the lifecycle of ethylene would be further reduced if emissions at the end-of-life are avoided. For instance, by selecting a different end-of-life technology or by coupling CCS with the incineration process. In that case, the lifecycle emissions of ethylene could reach negative values, as those of the cradle-to-gate approach (top axis in Fig. 4).

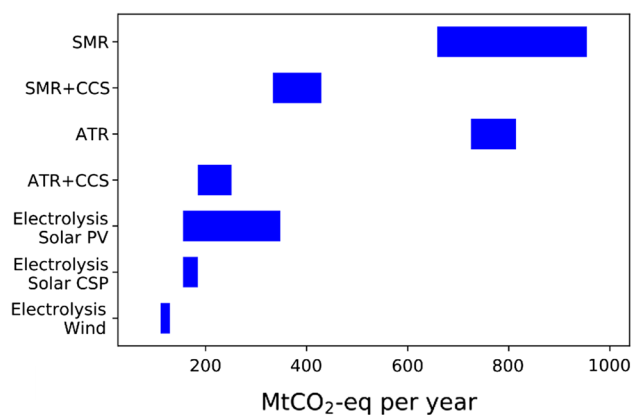
Regardless of the type of biomass feedstock, one of the biggest questions pertaining the exploitation of biomass in the chemical sector is the amount of resources required, which compared to energy demand is relatively small. Bos and Sanders [65] estimated the global production of chemicals to be between 1400 and 1700 Mt/y, of which about 300 Mt/y are based on naphtha. The production of chemicals from all fossil sources increases to more than 550 Mt/y and approximately 700 Mt/y would be required by 2030 [66]. Within the European context, Bos and Sanders [65] reported that production of organic chemicals would represent around 65 Mt/y, requiring a maximum of 554 Mt/y of biomass if the production route generates the same platform chemicals as the naphtha-based route. This value could be reduced to 315 Mt/y of biomass if functionalised molecules were produced, exploiting the biomass composition. If these values are extrapolated to satisfy the global demand of oil-based chemicals, and assuming a conservative crop yield of 8 t/ha, a total of 6000 Mt/y and 758 Mha/y would be required for the current platform chemicals route while 3500 Mt/y and 443 Mha/y would be required for the functionalised route. Taking the upper value as a reference, the production of oil-based chemicals would require approximately 46% of the global arable land (1500 Mha). While the use of second and third generation biomass can reduce the need for arable land, the amount of biomass required to guarantee a constant supply to the sector is still significant (up to 90 EJ/y).

Whereas biomass presents potential benefits to achieve even negative emissions in the sector, it is imperative to increase energy and conversion storage. The deployment of biorefineries to produce chemicals using high quality land is likely to compete with other land-based activities, such as food and bioenergy production, generating price pressures. An alternative is to increase the efficiency of this route by (i) breeding or modifying genetically plants to grow faster and produce more biomass, (ii) creating novel configurations of photosynthetic pathways to avoid inefficient steps, or (iii) using artificial assemblies to produce fuels or chemicals from water and CO₂ [23]. Yet, risks associated to biodiversity loss, increased biochemical flows, soil depletion, and erosion remain uncertain [50]. The sustainable use of biomass should also address the consumption of water, which relates to crop growth, pollution from fertiliser application, and use during the processing of the biomass.

3.3 Solar feedstocks: artificial photosynthesis

Another method for solar feedstocks or energy storage is to borrow the design of nature by breaking chemical bonds and to produce chemicals in an artificial photosynthesis process. These (photo) electrochemical processes are also referred to as artificial leaves [67–69]. The basic concept behind this idea is to use solar energy to split abundant species at the bottom of the free energy spectrum, such as CO₂, CH₄, N₂, and H₂O, and transform them into more complex molecules by means of solar energy, ideally at lower temperatures and pressures. This pathway can represent another way to electrify

Fig. 5 Annual CO₂ emissions released in the production of 75 Mt of hydrogen for current carbon intensities. *SMR* Steam reforming of natural gas, *ATR* autothermal reforming of natural gas, *CCS* carbon capture storage



the industry when electricity is directly used to make molecules. This power-to-chemicals approach has the potential to contribute to the transition from a fossil to a solar-based industry in the long term.

The most prominent example to date is found in water splitting. When analysing the energy involved in the process of generating solar fuels, it is observed that water splitting is the process where solar energy storage occurs. While the reversible potential for water splitting is 1.23 V, that of carbohydrate from water and CO₂ is 1.24 V. Therefore, the production of the carbohydrate stores only 0.01 eV more energy than water splitting, and carbohydrate production is nature's way to store the hydrogen released from water splitting [67]. Hydrogen production via water electrolysis is primarily observed as a way to store solar energy into chemical bonds, a process also referred as power-to-gas (PtG). This concept has been considered as the most cost-efficient solution for inter-seasonal storage and links electricity and gas networks with the chemical sector [70].

Water electrolysis can be performed in Alkaline Electrolysis Cells (AEC), Proton Exchange Membranes (PEM), or Solid Oxide Electrolysis Cells (SOEC). AEC electrolyzers are already mature with production capacities up to 60 kg/h. This is a very clean technique that can produce hydrogen above 99.5% purity using an alkaline medium (25–30% KOH). AEC systems operate at voltages of 1.8–2.4 V and temperatures of 60–80 °C, resulting in voltage efficiencies of 62–82% [71]. Their long stack lifetimes (60,000–90,000 h) and avoidance of noble metals make them relatively economic (\$1000–1400 per kW_e capex). Development of this technology focuses on increasing current density and operating pressure, which have a negative impact on the size of the system and hydrogen cost. Additionally, efforts are made on improving their dynamic operation, as it is still limited affecting their efficiency and gas purity [72–74]. PEM electrolyzers are based on the solid polymer electrolyte concept, in which the PEM separates two half cells, having the electrodes directly mounted on the membrane. The system produces hydrogen at higher purities than AEC, typically greater than 99.99% at rates up to 20 kg/h. The process is carried out at very corrosive acidic regimes, requiring noble metals (i.e. platinum group) for its construction. The use of these materials, on top of a reduced stack lifetime (20,000–60,000 h), make PEM electrolyzers more expensive than AEC, with reported capital costs in the range \$1500–2800 per kW_e. However, PEM electrolyzers have a higher power density and cell efficiency, provide highly compressed hydrogen (30 bar), and have more flexible operation (minimum load capacity from 0 to 10%). Development areas focus on reducing the amount of noble materials and complexity of the system given the high pressure and water purity requirements [71, 75, 76]. SOEC electrolyzers are a promising technology still at the research stage, although Sunfire already offers commercial reversible SOEC systems demonstrated at a small scale (1 bbl/day of diesel via Fischer–Tropsch). Their capital cost is estimated to be approximately \$4500 per kW_e. These systems use solid ion-conducting ceramics as electrolyte, which allows operations at significantly higher temperatures with high electrical efficiency and low material costs. SOEC systems can also operate in reverse mode as a fuel cell or in co-electrolysis mode producing syngas from water steam and CO₂. Overall, these systems present high potential for PtG and PtL applications. Current research focuses on avoiding material degradation by stabilising existing components, developing new materials, and reducing operating temperatures [73, 77].

The versatility and potential reduction of CO₂ emissions via water electrolysis have put hydrogen forward as a key component to achieve the decarbonisation of the chemicals sector, particularly through ammonia and methanol production [3, 33, 78–82]. The current production of hydrogen accounts for approximately 75 Mt per year and is responsible for 830 Mt CO₂ [83]. Around three quarters of current production come from natural gas, followed by coal and small amounts of oil and electricity. Fossil-based feedstocks are referred to as grey hydrogen, while their coupling with CCS technologies refers to blue hydrogen. The production of hydrogen from water electrolysis using renewable energy, such as solar PV

or wind, is referred to as green hydrogen. Steam reforming of natural gas (SMR) releases 8.9–12.9 kg CO₂eq/kg H₂ with the potential to be reduced up to 4.5–5.8 kg CO₂eq/kg H₂ if CCS is incorporated [84]. Autothermal reforming of natural gas (ATR) releases 9.8–10.9 kg CO₂eq/kg H₂ without CCS and 2.5–3.4 kg CO₂eq/kg H₂ with CCS. Water electrolysis has the potential to reduce CO₂ emissions to values as low as 2.0 kg CO₂eq/kg H₂ when powered by solar electricity and even lower with other renewable sources, such as wind (1.5–1.75 kg CO₂eq/kg H₂). Figure 5 shows the annual CO₂ emissions embodied in these routes for current hydrogen production. As observed, ATR + CCS and green hydrogen show the potential to reduce emissions beyond 600 Mt CO₂eq/y. The emissions of solar PV, however, still present large uncertainty. This is caused mainly by the module manufacturing process still heavily dependent on fossil fuels and variation of capacity factors across different regions [85].

Analysing current production costs, if we consider an alkaline electrolyser with an installed cost of \$1200/kW_e operating at full capacity, lifetime of 20 years, annual interest rate of 10%, and solar PV electricity of \$90/MWh, hydrogen production costs reach \$5.6/kg. From this, electricity represents \$4.7 while capital costs represent \$0.9. By 2050, installed costs of alkaline electrolysers are expected to decrease below \$500/kWh while levelised costs for solar PV electricity are expected to reach values around \$10–50/MWh [86]. Under the assumption of an electrolyser unit with the cost of \$500/kWh and electricity price of \$30/MWh, hydrogen would reach \$1.9/kg when operating at full capacity, from which \$1.5 come from electricity consumption and \$0.4 from capital costs. These results show that, from the hydrogen perspective and despite the progress and continuous development of solar PV electricity, efforts are still required to present hydrogen from solar PV as an attractive alternative in economic and environmental terms. While these improvements are attained, blue hydrogen could help in the transition toward a decarbonised sector. For instance, technologies like ATR coupled with CCS report costs of \$2.2/kg H₂ and emissions of 2.5–3.4 kg CO₂eq/kg H₂. This costs are well within the range of SMR (\$1.8–3.0/kg H₂) and slightly cheaper than SMR coupled with CCS (\$2.0–3.3/kg H₂) [87]. This strategy not only promotes the deployment of the hydrogen economy but also allows a decoupling of electricity generation and hydrogen production. This results in higher flexibility from the energy systems to produce either power or hydrogen, as the sector transitions toward green hydrogen production.

The deployment of CCUS coupled with solar-based hydrogen could bring significant benefits to the industry. This was demonstrated by Kätelhön et al. [66], who analysed the impact on CO₂ emissions that hydrogen coupled with CCUS could bring. In their analysis, they estimated the demand of 20 large-volume chemicals that will account for 75% of the sector's emissions by 2030. In the pathway proposed, CO₂ and hydrogen were transformed into methanol and methane, which worked as platform molecules. CO₂ was sourced from either a highly concentrated industrial source or direct air capture, and methanol was then transformed into olefins and aromatics, which worked as basis for the chemicals under study. The results reported a demand of 3.72 Gt CO₂ and 0.59 Gt H₂ (> 24 PWh of additional electricity) resulting in emissions from cradle-to-gate of – 0.9 Gt CO₂eq if solar energy was used as the source of hydrogen (1.3 Gt CO₂eq from cradle-to-grave) [66]. The amount of hydrogen required to satisfy this scenario is eight-fold current hydrogen production, and 59 Mt of hydrogen production should be deployed each year until 2030 to achieve this goal. If we assume AEC electrolysers producing 60 kg/h of H₂ operating at full capacity throughout the year, around 100,000 electrolysers would be required to satisfy such demand each year. This amount would double if we assume an electrolyser capacity factor of 0.5, and would triple in any scenario if we consider PEM electrolysers producing 20 kg H₂/h. Despite the maturity achieved in the water electrolysis market, the sector is still not ready to supply the number of electrolysers required. Furthermore, such deployment might result in other problems, like the need for very large equipment or facilities when dealing with AEC or scarcity of mineral resources in the case of PEM. However, the benefits in CO₂ emissions are clear, which along with the technological improvements and availability of cleaner and cheaper electricity are promising.

The potential benefits toward decarbonisation observed from water electrolysis have spurred the research of other electrochemical systems. For instance, CO₂ reduction into simple (CO and CH₄) and complex compounds (C2–C6), dinitrogen reduction toward ammonia, and partial oxidation of methane to methanol [69, 79, 88–92]. PEM electrolysers can still be applied for the transformation of CO₂ into CO and O₂. This CO can be further combined with hydrogen to produce syngas, which can in turn be transformed into other chemical blocks, such as ethylene, ethanol, or methanol. Opus 12, which relies on PEM electrolysers, claims it has been able to produce 16 commodity chemicals, working to scale-up its reactors over the next years [93]. SOEC electrolysers are also considered for the conversion of CO₂. These systems split water and CO₂ to generate CO and H₂ (syngas), which can be further used to produce fuels and chemicals. This concept has been demonstrated by Sunfire in Germany, with yields of 10 L per day of diesel using the Fischer–Tropsch process. Sunfire is scaling-up the technology with plans to start commercial operations in Norway next year, expecting to avoid 29 Mt CO₂ annually from fossil fuels.

Analysing the electrocatalytic conversion of CO₂ combined with water electrolysis, De Luna et al. [88] concluded that the production of CO, H₂, ethanol and ethylene is cost competitive when electricity has a cost below \$40/MWh and the efficiency of the system is above 60%. At electricity costs of \$20/MWh, formic acid, ethylene glycol, and propanol would also be feasible. Bolinger and Seel [94] showed that the levelled cost of power from solar plants will shortly reach \$40/MWh in the US, reaching the first milestone. Although average global costs are expected to reach this value by 2050 [86]. In terms of system efficiency, both alkaline and PEM electrolyzers have reached the second milestone for water electrolysis. However, this milestone still represents a challenge to overcome in other less mature electrocatalytic systems. Analysing the state of the art of four different electrocatalytic routes, Martin and Perez-Ramirez [69] determined the feasibility of these systems on the basis of five different figures of merit: energy efficiency, activity, overpotential, selectivity, and stability. They concluded that water electrolysis has achieved maturity, followed (far behind) by electrocatalytic reduction of CO₂, with N₂ and methane still at a very early stage. However, they also pointed that electrocatalytic requirements can be less demanding as transportation costs, available solar radiation, and target products are considered.

3.4 Summary of solar technologies

Here, we present a summary of the status of the solar technologies addressed in this section, starting with energy generation and storage, followed by biomass, and finally presenting electrocatalytic routes including hydrogen production.

3.4.1 Electricity

- Direct implementation of electricity via PV, perovskite panels, or CSP with potential abatement of CO₂ emissions from 500 to 140 Mt CO₂/y for current electricity consumption (6 EJ/y) and solar electricity with carbon intensity of 0.085 kg CO₂/kWh.
- Solar PV and CSP average costs of \$90 and \$270/MWh with capacity factors of 0.13–0.23 and 0.33, respectively.
- Most polluting technology among renewables given its dependence on fossil fuels during manufacture of panels. Solar perovskite expected to reduce costs and environmental impact given its reliance on cheap and abundant raw materials. In all technologies, worsening of land occupation and consumption of bulk materials like iron, copper, and aluminium.

3.4.2 Heat

- Solar systems already operating at temperatures between 60 and 250 °C, representing already 50% of industrial heating in the most energy-intensive sectors. Solar CSP able to provide temperatures beyond 400 °C.
- Power-to-heat expected to be the first type of electrification to implement in the chemical sector. Some technologies available include resistance and induction heating, heat pumps, microwave processing, electric boilers, and industrial furnaces. Given that capital costs and efficiencies are similar to conventional fossil fuels, implementation dependent on feasible costs.

3.4.3 Energy storage

- Alternatives include electrochemical storage (batteries), pumped hydropower, or thermal storage.
- Electricity storage still expensive with potential environmental and social impacts, such as those related to lithium mining.
- Thermal storage systems include sensible heat storage, latent heat storage, and thermochemical storage (chemical bonds). Thermochemical storage of particular interest as energy vector can also be used as raw materials (e.g. biomass, hydrogen, ammonia, or methanol).

3.4.4 Bioenergy with carbon capture and storage (BECCS)

- Alternative to generate energy and fuels at negative emissions.
- Only few BECCS facilities operating although technologies required are already mature.
- Carbon efficiencies of 17–38% for energy generation and 45–50% for biofuels with costs of \$20–300/t CO₂ avoided.

3.4.5 Biomass as feedstock

- Its use represents the direct consumption of naturally stored CO₂, representing an attractive option for processes difficult to decarbonise throughout its entire lifecycle, like ethylene/plastics and ammonia/fertilisers. Potential to achieve negative CO₂ emissions if end-of-life routes are able to capture/recycle CO₂.
- Versatility to produce a wide range of chemicals and fuels. However, highly integrated refineries and higher efficiencies will be required to fully exploit its composition, reduce land competition and resources consumption.
- Biomass residues can present cost-competitive options 30–60% more expensive than those from conventional routes. Expensive feedstocks (e.g. dedicated crops) are less attractive, with costs above three-fold compared to fossil-based options.
- Cost and environmental impact heavily dependent on factors like source of biomass, technology, and location.
- Competition against food in some markets can influence its supply, with still uncertain risks associated to biodiversity loss, increased biochemical flows, soil depletion, and erosion.
- Concept based on the use of solar energy to split abundant species such as CO₂, CH₄, N₂, and H₂O.

3.4.6 (Photo) electrocatalytic processes as solar feedstocks

- Production of energy vectors that can also be used as feedstocks (hydrogen, ammonia, methanol, etc.).
- Technology expected to play a prominent role in the long-term as solar energy becomes widely available at lower costs.
- Potential to deploy distributed systems, of particular benefit to regions with little or no infrastructure.

3.4.7 Hydrogen production from water electrolysis

- Production costs still at least 2.5 times more expensive than conventional routes coupled with CCS (blue hydrogen) (\$5.6/kg for alkaline electrolysis vs \$2.0–2.2/kg for SMR and ATR+CCS). Expected to become cost-competitive by 2050, when costs approach the barrier of \$2/kg.
- CO₂ emissions currently competing against those of blue hydrogen via ATR+CCS (2–5 kg CO₂eq/kg hydrogen). Further reductions expected as electricity mix decarbonises.
- In combination with CCUS, potential to attain – 0.9 Gt CO₂eq in the production of 20 major chemicals from cradle-to-gate. This would require 3.72 Gt CO₂, 0.59 Gt of hydrogen, and > 24 PWh of electricity.

3.4.8 Other electrocatalytic technologies

- Research in processes like CO₂ reduction into simple and complex compounds, dinitrogen reduction to ammonia, and partial oxidation of methane to methanol. Level of maturity of different electrocatalytic routes: H₂O >> CO₂ ≥ N₂ > CH₄.
- Low electricity costs (below \$40/MWh) and high system efficiencies (above 60%) required to attain cost-competitive chemicals.
- Opus 12 claims the production of 16 commodity chemicals via PEM electrolysis and Sunfire (Germany) used SOEC in the conversion of CO₂ to fuels (diesel) via the Fischer–Tropsch process.

4 The role of PSE and LCA to support decision making toward a decarbonised solar-based chemical sector

In the previous section, we presented the main applications and advances of solar energy and feedstocks in the context of the chemical industry. We highlighted the need for continuous improvements able to provide solutions at feasible costs for the sector and showed the potential to reduce CO₂ emissions. While the primary focus of the sector is to attain a decarbonised industry, we also pointed to unintended environmental burden shifting for some of the technologies available. In this section, we now discuss how these technologies can be deployed within the current structure of the chemical industry based on sustainable development with considerations beyond CO₂ emissions. To attain this task, we first make a case for PSE and LCA to assess new and innovative solar processes at a multi-scale level, pointing to their key role to understand the complex interactions between industry, society, and ecosystems. On this basis, we next analyse

how this framework can support the decision-making process to deploy solar technologies in combination with other strategies identified to decarbonise the sector while observing other aspects of sustainable development.

4.1 PSE and LCA as a framework to assess sustainable development

PSE has traditionally offered solutions to support the decision making of the chemical supply chain, from the molecular to the enterprise level [95–105]. Through the development of powerful tools in the analysis, design, synthesis, simulation, optimisation and integration of processes, PSE bridges gaps between atomistic, mesoscopic, and macroscopic levels. This multi-scale level is observed in the inclusion of results obtained from smaller scales that are incorporated in larger spatial and length scales or integrated frameworks that span two or more scales in time and length [95, 96]. For instance, computational chemistry and computer aided molecular design (CAMD) work at the molecular level to guide experimental procedures, reaction engineering, and process performance [98–101]. At the process level, PSE addresses energy and process efficiency through techniques such as heat integration, waste energy recovery, or process intensification [102, 103, 106]. As technologies are scaled-up, enterprise-wide optimisation looks at multiple levels of operation, being able to define long-term investments through medium- and short-term decisions at the planning, scheduling, and control level [97].

Traditionally, PSE tools are applied to assess economic performance. Through models able to characterise mass and energy balances, define process topologies and supply chain networks, PSE tools allow the quantification of financial metrics based on the capital and operating costs of a process [96, 97, 101–103, 106]. In the environmental facet of sustainable development, LCA has become the main framework to assess environmental impact [105, 107, 108]. The basic concept of LCA is to capture mass and energy flows exchanged with the environment during the life cycle of a product. As a result, this approach goes beyond a sole analysis of CO₂ emissions and allows the quantification of environmental impacts across different categories. This is relevant to assess the environmental footprint of the chemical sector, which is known for releasing a myriad of elements into air, water, and soil, and consuming vast amounts of energy and resources. The structure defined by the International Organization Standardization (ISO) [109, 110] to implement an LCA includes four stages: (i) goal and scope definition, which also defines the reference product (i.e. functional unit) and system boundaries of the study; (ii) life cycle inventory (LCI), which recollects all the inputs and outputs of the reference product; (iii) life cycle impact assessment (LCIA), which translates the inventories into environmental impacts; and (iv) interpretation of the analysis. Given its holistic approach, the collection of data to define the LCI of a product involves a vast number of processes resulting in a large amount of data. Typical data sources involve industrial data, LCA databases, process models or laboratory data, and streamlined LCA approaches [111–113], with the uncertainty of the data increasing as we move down the list.

While PSE naturally serves to the purpose of multi-scale modelling and optimisation to support decision making, LCA shares its systems thinking and is based on the same mapping and measurement approaches. Therefore, the incorporation of LCA into PSE to measure resource consumption and environmental impact becomes straightforward from the conceptual point of view. As this framework is applied to screen alternative solutions, it allows the identification of technical barriers and, ultimately, enable the efficient allocation of resources and a fast deployment of the most performing options. A thorough review of the application of LCA for the design of chemical processes can be found in Kleinekorte et al. [107] and Guillen-Gosalbez et al. [108]. At the molecular level, this framework has recently reached CAMD applications, particularly focused on solvent performance in processes such as CO₂ capture or Rankine cycles [101, 114, 115]. At the plant level, a broad range of studies have been published to improve process performance and assess production routes of chemicals from biomass or electrocatalytic routes in combination with CCUS [33, 50, 55–58, 78, 79, 81, 82, 105, 116]. At the supply chain level, network models based on superstructures have been developed to (i) capture the highly integrated status of the chemical sector [7, 95, 113, 117–119]; (ii) identify synergies among processes in which emerging technologies can be integrated [7, 55, 60, 120, 121]; and (iii) identify interactions between technologies and resources at local or multi-regional regional levels to promote an efficient use of resources [122–126].

The vast amount of studies combining the tools provided by PSE and LCA attest to the benefits of this approach, which provides a powerful framework to gain a better understanding of novel technologies considering sustainability from the molecular to the global level. However, the assessment of emerging technologies is subject to multiple sources of uncertainty arising from lack of data or data inaccuracy [107, 127]. Therefore, quantifying and understanding the sources of uncertainty is crucial to provide reliable assessments. While parameters and models carry levels of uncertainty, other sources of uncertainty pertain to modelling choices, most of them also influenced by spatial and temporal variability. For instance, mass and energy balances in a reaction can derive from punctual experimental results or equilibrium

calculations given the lack of a robust kinetic model. Similarly, shortcut models can be used in the calculation of process units, such as distillation columns or membranes. The economic evaluation includes uncertainties of prices for raw materials and energy inputs as well as assumptions related to technological learning across time and space [107, 128]. In terms of LCA, uncertainties might come from inventory data, as previously described. However, other sources of uncertainty stem from the lack of knowledge regarding the environmental impact that specific chemicals have over the environment. For instance, the early assessment of biofuel production focused on CO₂ emissions and ignored impacts over land use or potential waste generated by the side products. At some extent, this is still the case for most assessments seeking to reduce CO₂ emissions without accounting for other effects, such as water consumption, mineral scarcity, ecotoxicity, etc. As solar technologies are deployed at large scale, their effects over the environment might only be revealed after time, with new impact categories being continuously developed. In this context, multiple authors have presented methodologies to quantify uncertainty either through stochastic or analytical assessments [127, 129–131]. And while there is a consensus agreeing on the relevance of accounting for uncertainty in the assessment of emerging technologies, this is still not a common practice. Ultimately, this approach is key to provide a holistic view of the chemical sector and its gradual transition away from fossil fuels. Furthermore, such approach is vital to address practical hurdles, set performance targets, and better inform policy, government, and business bodies taking into account the short, medium, and long term elements involved in the large-scale deployment of solar technologies [3, 4].

4.2 Opportunities for PSE and LCA to support decision making toward a solar-based chemical industry

Research has shown that solar energy can be generated in a cost-effective manner with silicon, stored in the form of chemical fuels from hydrogen, or stored as biomass and do so at efficiencies well beyond that of nature [22]. These discoveries raise hope to move from an industry based on fossil carbon to one based on solar energy and renewable sources. The reductions in manufacturing costs of solar panels, batteries, and other carbon-neutral technologies attests to the power of investment in R&D and innovation. This will ultimately provide better options to deploy clean energy systems than those available to date. Despite this progress, there are multiple barriers to deploy solar energy and feedstocks within the chemical sector. While some still refer to technical challenges, some others point to hidden costs, lack of information, and availability of capital [132]. As we move away from the current structure of the chemical industry based on fossil fuels, the goal of carbon neutrality will require the combination of additional factors. These include energy improvements, circular economy, CCS, biomass and hydrogen as feedstocks or energy sources, with other technological breakthroughs expected to gain relevance as they achieve maturity (e.g. second-generation biomass or novel electrocatalytic routes) [3, 13, 14, 133–137]. In this context, the framework provided by PSE and LCA will be essential to identify optimal pathways where basic science and engineering work together across industry and academy.

4.2.1 Solar electricity and heat

Looking at energy savings, the roadmap to decarbonise the world's chemical sector toward 2050 provided by the IEA [9] indicated energy savings of 5–15%. In their analysis, they evaluated 57 processes built on best practice technologies, which are economically viable technologies at industrial scale. Within the European context, Cefic [137] reported that energy savings of 20% for ammonia production and 14–21% in cracker products could be achieved in 2030 by implementing readily available technologies. However, despite these potential savings, without accounting for changes in feedstocks, the increased demand of chemicals in the coming decades would result in a 25–39% rise in energy consumption with a 15% fall in CO₂ emissions if accounting for energy improvements and CCS [138]. The integration of solar electricity into the chemical industry to decarbonise heating is still distant as most of its deployment is used into the electricity grid. Once solar energy reaches the deployment required to be incorporated into the chemical sector, it will still require innovative solutions, primarily related to guarantee the supply at feasible costs [40, 46]. While some alternatives have been reported, their industrial implementation is still to be demonstrated [36–38]. Here, regional assessments based on a process systems thinking are essential to identify locations in which the availability of solar energy can be cost-competitive. This can also alleviate the challenge to find the most efficient way to tackle the intermittency of solar energy at minimum costs. Electricity storage still remains expensive and while the ability to transform electrical energy or heat into chemical bonds provides a cheaper alternative, the energy vectors and technologies identified cannot compete with fossil-based alternatives (e.g. hydrogen, ammonia, or methanol) [43]. Models at the supply chain level can help to elucidate attractive routes for the production of chemicals or fuels from these energy vectors.

4.2.2 Solar feedstocks

In the feedstock context, the use of biomass represents the most mature option, being able to abate both the emissions on site and the emissions of the produced commodities. The ability of biomass to provide CO₂ captured from the air presents an appealing alternative to processes difficult to decarbonise throughout their life cycle. Examples refer to the supply chain of ethylene and plastics or ammonia and fertilisers [54, 62, 139, 140]. However, its deployment will depend on the availability of the resource, locations for carbon storage, or economically feasible networks able to guarantee their operation. In addition, biorefineries to produce chemicals using high quality land are likely to compete with other land-based activities, such as food and bioenergy production, generating price instabilities [23]. While advanced biorefineries, related to the use of more sustainable biomass (e.g. lignocellulose), might represent a solution, the technical feasibility of their routes to produce fuels and chemicals carry large uncertainty, as they are still in the R&D, pilot or demonstration scale [55–59, 141, 142]. Similarly, risks associated with biodiversity loss, increased biochemical flows, soil depletion, and erosion remain uncertain [50]. At present, electrocatalytic processes also present technical and economic challenges. While they are observed as technologies that can abate CO₂ emissions of the sector in the long-term, most of these technologies are still at the research stage [69, 88]. Apart from water electrolysis, the technical feasibility at the electrolysis, process, and supply chain levels are still to be demonstrated. And even in the case of green hydrogen, which is considered a mature technology, electricity prices and capital costs still need to be reduced further to generate cost-competitive products [3, 88]. As these technologies are developed, it is essential to make use of cheap and abundant materials in their construction, avoiding expensive and rare materials which might hinder their large-scale implementation. This will be reflected not only in production costs but will also prevent burden shifting across environmental categories, particularly those related to mineral resource scarcity.

4.2.3 Structure of the sector

A deep integration of solar technologies within the current structure of the chemical sector is essential to reduce investment costs as well as guaranteeing development of local environments and societies. Given the complexity of the chemical sector, such development should be based on a national basis, guaranteeing the supply of chemicals demand according to local resources availability and societal needs. The chemical industry of each country has its own distinctive historical background, structural characteristics, access to resources (fossil and non-fossil), and decarbonisation options. After this scenario has been understood, this approach can then be extended across multiple locations to address trans-regional hurdles. As the use of solar energy and feedstocks become available, an additional challenge to meet will be that of their integration into such regional structure. At present, oil and natural gas facilities form the backbone of the industry. According to the IEA [143], fossil fuels are still expected to continue to be the basis for the chemical industry despite the risks associated with a slow transition. These facilities are highly centralised systems that include extraction, distribution, and handling of fossil fuels, requiring equally large transformation plants (refineries). Their maturity and complex integration present reduced opportunities for innovation due to large costs that changes may induce. In this context, solar energy equipment has the significant advantage that the small scale of the equipment also makes the time required from initial design to operation short. Therefore, any improvements can be easily identified and incorporated quickly into modified designs or processes [144]. This also presents the opportunity to deploy processes entirely driven by solar energy suitable for small scale production, representing a paradigmatic societal change as we move away from centralised thermally-based systems to distributed arrangements [69, 80]. Such distributed configuration allows instead a much better integration into local economies, including aspects related to circular economy. This could play a crucial role in developing and surviving economies, in which the decarbonisation of the sector might not be a priority and large investments seem risky. As a result, the chemical industry would promote the generation of jobs, development of local economies, and an overall progress rooted on sustainable grounds.

4.2.4 The economy and the environment

While the reductions in CO₂ emissions that solar energy and feedstocks provide are evident, such improvements will result in increased energy demand, production costs, and other environmental impacts. Analysing the transition to decarbonise ethylene and ammonia toward 2050, Pee et al. [3] reported an increase of 4–ninefold in electricity consumption for power and hydrogen generation, in addition to 8–42 EJ of biomass per year. Their solutions included technological efficiency gains and CCS, requiring investments from \$1.2–3.3 trillion, resulting in cost increments by 5–35% for ammonia

and 40–50% for ethylene. They also reported electricity costs below \$35/MWh would make hydrogen use in ammonia production more cost-competitive than implementing CCS to conventional routes. In the case of electrification of heat in ethylene production, electricity costs of \$25/MWh are a better alternative to CCS. These electricity costs, however, are still far from current global average prices of \$90/MWh, although it is expected that prices in those ranges could be attained by 2050 [86]. Such cost increases pose threats to the competitiveness of a region under fragmented global environmental policies and calls for global action and a deeper integration of the supply chain of the sector. This was pointed out by Cefic [137], who reported that the isolated implementation of environmental policies to tackle CO₂ emissions in the European Union might cause the industry of the region to struggle as it competes against reduced prices of regions like the US or Asia. They also concluded that it was essential that the energy and climate policy framework in the EU stimulates sustainable and efficient growth.

The cases presented in this perspective suggest that the transition toward a carbon-neutral industry will come at the expense of increased costs, and therefore, an environmental policy framework that promotes sustainable development will be required. In contrast, fragmented regional actions will pose threats to the competitiveness of the industry across different areas. As this policy framework is conceived, care must be placed in continuously analysing the environmental footprint of the chemical sector. While solar technologies show a significant abatement of CO₂ emissions, effects are being observed over land use, mineral scarcity, biodiversity loss, water consumption, among other categories. It is therefore important that the models and analytical tools developed are based on our increasing understanding of the impact that such effects might have over the economy, environment, and society. In such a way, we will be able to support the decision-making process to attain a sustainable solar-based chemical industry. However, a deep integration between basic science and engineering will be essential to reduce uncertainties, improve process performance, and better inform policymaking and stakeholders.

5 Conclusions

The implementation of solar technologies into the chemical industry has the potential to significantly reduce the carbon intensity of this sector. After analysing the transformation of sunlight into electricity, heat, and chemicals, a general perspective to achieve this goal can be presented. In the short term, first generation biomass conversion could be implemented to promote a solar-based industry along with more energy-efficient technologies and CCS. In the medium and long run, electrification of heat, lignocellulosic biomass conversion and hydrogen from water electrolysis present options that could reduce further the emissions of the sector. Envisioning the long-term future of the chemical industry, as solar electricity becomes available at lower prices, (photo) electrocatalytic systems deployed in a distributed fashion present an attractive option that can exploit the regional abundance of solar power in combination with other renewable resources.

Renewable energy is still not yet deployed at a scale to decarbonise industrial production and intermittency remains as a key issue. The use of solar and renewable energy in the sector also seems distant, as the power sector must be first decarbonised and production costs associated with electrification cannot yet compete against their fossil-based counterparts in most applications. For these reasons, fossil fuels are still expected to be the basis for the chemical industry in the coming decades. From the alternatives presented to promote a carbon neutral scenario, a combination of strategies will be required to transition to a carbon neutral sector. While biomass seems to be the only solar technology contributing at present with the decarbonisation of the sector, the inclusion of hydrogen from water electrolysis as feedstock could further reduce its emissions. Even if the installation of large-scale water electrolysis presents a challenge, such transition can be promoted with technologies such as ATR coupled with CCS, resulting in slightly larger CO₂ emissions than those of green hydrogen powered with solar PV at current emissions of solar electricity.

The use of solar energy is a general trend that is widely accepted in the chemical and other industries. A sharp rise in supplies of solar, wind, and other forms of renewable electricity lies behind the trend. In 2018, the world surpassed 1 TW of installed solar and wind capacity. The second TW is expected by mid-2023, at just half the cost of the first, and the pace is likely to accelerate. In this context, the concept of electricity-to-chemicals will play a significant role to drastically reduce the emissions of the sector, as simple abundant molecules are transformed into chemicals and fuels using renewable energy. Most of these systems are still at very early stages of design, and significant progress is still required to develop catalyst systems, engineer reactors able to process high mass fluxes, and separation units that efficiently integrate solar power. Electrocatalytic systems also present the opportunity to change current practices of the sector, moving from centralised to decentralised facilities able to promote sustainable development and equity at different economic levels.

Most of these technologies will have to compete with an industry that has invested over a multitrillion dollar infrastructure over the last century. Therefore, the transition requires policies and societal changes that affect consumer behaviour in addition to technology improvements and innovation. Furthermore, the reduction of CO₂ emissions will result in higher production costs and will very likely incur damage to other elements of the ecosystem, such as land occupation, water consumption, or mineral resources. Although the primary focus of tackling emissions of the sector is well placed, care must be placed in all these other instances to avoid shifting one problem into a new one. While a solar-driven industry is part of an ongoing transition to a new economic and environmental status of the sector, its commercial implementation will ultimately rely on its economic feasibility based on rigorous techno-economic and environmental assessments in which the analysis of evolving economic, social, and political drivers are included. A process systems engineering thinking in combination with life cycle assessment present a powerful approach to assess this complex scenario. This methodology observes the interaction of raw materials and technologies availability along with the dynamic behaviour of the economy and response to policies, which will ultimately dictate whether it is feasible to conceive a solar-based chemical industry.

Authors' contributions AG-G wrote the main manuscript text. NMD and NS revised it critically for important intellectual content. All authors read and approved the final manuscript.

Declarations

Competing interests The authors declare no competing interests.

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