



Green synthesis and sustainable processing routes

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Abstract

This perspective analyses last year's trends in green synthesis and sustainable processing routes from the viewpoint of the leading emerging industrial directions and needs. After briefly introducing the future scenario, the aspects discussed regard carbon neutrality and defossilization of the chemical industry, electrification of the processes and introduction of low-carbon H₂ routes. Some elements of artificial leaf and solar-to-X technologies, as well as e-chemistry, are also discussed. Trends, opportunities, and personal concerns regarding some directions are presented. The aim is to give clues to analyse this complex topic rather than offer a state-of-the-art and in-depth discussion of the presented examples.

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Keywords

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Introduction

The term “green synthesis” has become of increasing popularity in the last decade, with the number of publications containing these words (in title, keywords or abstract) rising from 511 in 2013 (articles + reviews) to 3696 in 2023 (of which, 367 reviews), according to Scopus database. Let's compare it to the 2023 year “green process” results. The numbers are drastically lower (385) and even lower for “sustainable process” (only 199 chapters of books, no articles or reviews).

These numbers underline a question for the area of “Green and Sustainable Chemistry”. There is a

significant academic interest in addressing the famous twelve principles of green chemistry (12 GC) and/or related metrics. Even if introduced around 25 years ago, they are still primarily presented as the key aspects on which RDI (research, development and innovation) should focus. However, do they have a practical impact on transforming chemical processes? The much lower numbers (replacing “synthesis” with “process” as search terms) pose a question mark on this aspect.

Most of the 12 principles of green chemistry find practical industrial applications in fine/speciality chemicals and pharmaceutical product syntheses [1,2] because they primarily derive from an evolution of chemical (organic) synthesis. Extensive industrial chemical processes for producing base chemicals and intermediates, which account for most of the world's production, base their current and future evolutions on aspects different from those indicated by 12 GC or that, when coincident, are for other motivations. Most large chemical processes use catalysis, but not to comply with the nine of the 12 GC. It is possible, if not uneconomical, to operate with a catalyst in a large-scale industrial process. Preventing waste (first of the 12 GC) is done because waste represents a cost.

The chemical industry faces significant issues that will likely transform soon [3]. There are socio-political targets, such as reducing greenhouse gas (GHG) emissions, but other motivations drive this industrial transformation, as commented below. Analysing the transformation from a 12 GC perspective will not result in a proper understanding of the motivations, trends and opportunities. For example, the electrification of chemical production for a progressive substitution of fossil fuels (FFs) as energy and carbon sources [4] cannot be adequately discussed in terms of the 12 GC. Thus, analysing emerging trends in green synthesis and sustainable processing routes requires a different approach.

The practical driving force for the ongoing radical change in chemical industrial production relies only partly on ecological or social motivations [3]. Even if sustainability reputation is relevant for companies, the primary motivations fostering the change to substitute FFs in chemical production are (i) the geopolitical pressure to overcome the limitations related to the large monopoly of FFs production and distribution, (ii) the change in the nexus between energy and chemistry (due to increasing competition of renewable energy) and its impact on the

availability and costs of raw materials for chemical production, and (iii) the modification in the economics of the overall value chain, due to increased competitiveness of renewable energy sources, and the loss of profitability windows in the petrochemical value chain.

Therefore, at least from an industrial perspective, the analysis of green synthesis and sustainable processing routes should be addressed differently than those based on 12 GC [5]. Similarly, using green metrics is becoming increasingly relevant when comparing the “greenness” of new solutions [6]. However, sustainability metrics and conventional techno-economic assessments cannot correctly catch the industrial driving forces behind the ongoing industrial transformation.

New investments in chemical processes and plants already account for this transformative scenario, even if there is still a considerable debate about whether and when a massive shift from an FFs-based to a renewable-based economy will occur [7,8].

This contribution analyses last year’s emerging trends regarding green synthesis and sustainable processing routes from the above perspective. This is a broad topic. Thus, only selected aspects will be commented on. They are organised according to the main industrial reasons behind the development rather than from more conventional viewpoints, such as those based on 12 GC [9]. According to the requirements for these contributions (having constraints in words, figures, references, etc.), this paper aims to describe the emerging trends concisely rather than analyse the state-of-the-art or thoroughly discuss the highlighted aspects.

Achieving carbon neutrality

Realising this challenge is a relevant driving factor determining the emerging trends in chemical production [10], although motivations are only partly related to reducing GHG emissions, as outlined above. This challenge requires a complex approach based on inter-connecting many innovative technologies, from renewable energy production, storage and transport to waste valorisation and Carbon circularity (C-circularity) [10–12].

Several studies analyse the status and strategies for defining the path to Carbon Neutrality (CN) [13–15]. Achieving the CN goal requires combining multiple sectors, from those characterised by hard-to-abate (energy-intensive) emissions [16] (including chemical production) to sectors with a negative footprint, such as bio-sequestration. However, properly balancing carbon-positive and carbon-negative sectors is more complex. In addition, it may be questioned whether technologies considered carbon negative by reports such as that made by IPCC (Intergovernmental Panel on Climate Change), e.g., Direct Air Capture with Carbon Storage

(DACCS) or the use of biomass to produce Bioenergy combined with Carbon Capture and Storage (BECCS), are effective in delivering negative emissions and be considered as sustainable technologies [17]. A primary objection is that these technologies, based on CO₂ storage, maintain linearity in carbon use rather than promote C-circularity.

Realising C-circularity, particularly in energy-intensive industries [16], is thus a main emerging direction towards CN. However, it is often considered an integration (rather than substitution) of the main action of carbon sequestration [18,19]. For example, Hu et al. [19], in estimating global CO₂ mass flows (in Gtons), indicate 10.9 Gtons CO₂ being stored against 3.1 Gtons used (for chemicals from urea to methanol, aromatics and olefins) in a high-emissions scenario (3.4 vs. 2.2 in low-emissions scenario). However, this estimation does not consider the capability to develop and industrially apply novel technologies to enhance C-circularity or the negative environmental impact of carbon storage technologies [18].

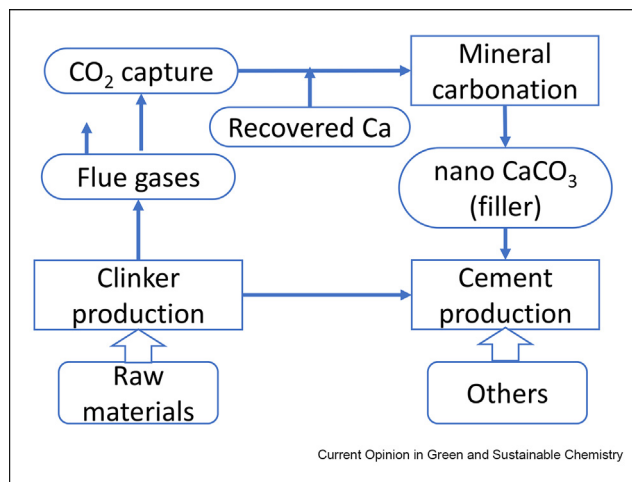
The bottleneck is the capability to accelerate the technological implementation of novel routes for C-circularity. This would require identifying the factors limiting innovation. Technologies for C-recycling may be broadly differentiated between those for recycling the material itself (either directly or via depolymerisation in the case of plastics) or those that recycle the carbon via CO₂ or other chemical intermediates). Being CO₂ the product of the dominant use of FFs, i.e., as an energy source, recycling CO₂ is thus a major element in achieving C-circularity.

Is it possible and feasible to use CO₂ in industrial practice? To have a significant impact, the technology should i) produce base chemicals (olefins, aromatics, etc.) because this would affect the downstream value chain and ii) use renewable energy for the uphill energy conversion of CO₂ [3]. In addition, CO₂ recycling should be integrated into the sector’s value chain to be effective and economical. Producing methanol from CO₂ emissions of steel manufacturing, as in many projects (Carbon2Chem® project in Germany, for example), generates a chemical/fuel with use and market out of the core interests of steel manufacturing. Producing CO, which can be used in blast furnaces, is a better alternative [16].

Similarly, CO₂ from cement production can produce additives, such as nano-CaCO₃ powders, which act as strength enhancers and accelerators of the cement hydration rate. Figure 1 illustrates the simplified scheme of this technology [20].

Chemicals such as formic acid are used as hardening acceleration promoters and grinding aids. In that case,

Figure 1



Simplified scheme of cement production with CO₂ recycling via nano-CaCO₃ filler production. Estimated reduction in CO₂ emissions by LCA up to 69% in Original Portland Cement production. Adapted from Ref. [20].

there is a boosting effect [16]. Part of the emitted CO₂ is recycled, but especially the products of CO₂ recycling are used to reduce the cement production's energy intensity (and thus CO₂ emissions).

These examples remark that estimating the impact as the amount of "sequestered" CO₂ (as the common practice) is incorrect. Still, the impact of the technology on the entire value chain should be considered. However, the process has to be economical because it is unfeasible that it can be applied if it leads to higher costs [21].

What are the critical elements of costs? The first is the capture/purification of CO₂. It may be made using technologies such as amine adsorption. Direct capture from the air (DAC) is feasible, but costs are high, even in energetic terms [22]. However, it is possible to consider technologies based on functionalised membranes. They allow CO₂ conversion technologies (for example, by electrocatalysis) to be coupled directly with CO₂-containing emissions or air. This solution can selectively capture CO₂ without requiring a preliminary capture/purification system [23]. While this could be a disruptive technology in implementing CO₂ recycling for C-circularity, it is surprising how scarce attention has been given to this aspect in front of such a large number of studies on CO₂ electrochemical conversion (as an index 78 reviews in 2023 on this topic).

The CO₂ conversion technology has to be driven by renewable energy. There are two possibilities. One is indicated as power-to-X (PtX) technologies (or e-fuels,

electrofuels), in which H₂ is produced first by electrolysis and then H₂ is used in thermocatalytic processes to produce chemicals or fuels (often in multiple steps). H₂ is a high-energy chemical. Its reaction with CO₂ (to give methanol, for example) led to a loose part of (chemical) energy stored in H₂. Only about 60% of the energy in making H₂ is typically retained in methanol. In addition, if the energy losses in producing H₂ by electrolysis are accounted for (typically 75% energy efficiency) and the energy losses in coupling electrolysis with the thermocatalytic process (by also considering the thermodynamic limitations associated with exothermic reversible reactions), the final overall energy efficiency of the PtX technologies is less than 40%.

It may be argued that H₂ can be used directly to avoid CO₂ emissions. However, energy costs associated with transporting and storing H₂ negatively influence the estimated energy efficiency for the whole value chain [24].

There are multiple potential advantages of solar-to-X technologies (or solar fuels). A better intensification and energy efficiency not passing through forming molecular H₂ derive from the direct use of solar energy. While better data would be necessary to prove these concepts, it emerges that a strategy to accelerate the development of technologies for recycling CO₂ is to foster the implementation of these technologies without passing through PtX deployment, which is instead the focus at the industrial scale.

A detailed discussion of pros/cons would not be the aim. However, the above elements remark how CN requires a wider-mind approach than those currently used. For example, Kätelhön *et al.* [25] indicated that CO₂ reutilization in the chemical industry can reduce GHG emissions by up to 3.5 Gt CO₂-eq. in 2030. However, it will require up to 55% of the projected global electricity production in 2030, e.g. about 18.1 PWh of low-carbon electricity. This is considered unfeasible. However, this estimation does not account for the possibility of distributed production through direct solar-to-X technologies, thus not requiring dependence on external low-carbon electricity sources. However, this study [25] remarks how cradle-to-grave (LCA) GHG emissions range from 300 to 100 gCO₂-eq/kWh for current and projected electrical energy taken from the grid. CN in chemical production cannot be achieved without directly developing solar-to-X technologies using renewable energy (RE), e.g., not mediated from the grid.

What emerges is that despite the intense research on green synthesis and sustainable processing routes and their claim to contribute to meeting the target of achieving CN, a clear definition of ranking priorities,

gaps, and bottlenecks is missing. This determines the slowness in moving from R&D to innovation.

Defossilization of the chemical industry

Carbon-intensive industries, such as the chemical industry, are actively searching for solutions to decarbonise (better defossilize) their production [3,4]. This objective may appear equivalent to the first (achieve CN) but must be discussed separately because these aspects directly impact chemical production transformation. In addition, it impacts the socio-environmental objective of decoupling economic growth from resource use.

The increasing fluctuations in resource prices (energy, materials) force a resilient strategy based on exploiting, at best, the local resources. This is possible only by changing the growth model (in the chemical industry) from a centralised production and large-scale distribution to a distributed (decentralised) model based on local energy/materials resource use [26].

This would require a disruptive change in production technologies and the parameters for optimisation and evaluation (such as economy of scale). Decentralised technologies should use RE and local raw materials (including waste) directly, have a low-cost design, achieve process intensification and be reliable for non-technical users. The pros are shorter lead times, lower transportation costs, elimination of dependence on externalities, better flexibility, and lower supply chain risk.

Artificial photosynthesis is emerging as a promising and sustainable approach for decentralised production. These devices can provide a steady supply of renewable carbon (fuels and chemicals). They are indicated as

artificial leaves (AL) or trees. Their development is now at a Technology Readiness Levels (TRL) 4–5, although mainly for simple reactions (water splitting). In contrast, more challenging reactions such as CO_2 and N_2 reduction still require more R&D [27]. More than 10% of solar-to-chemical conversion efficiencies have already been achieved [28].

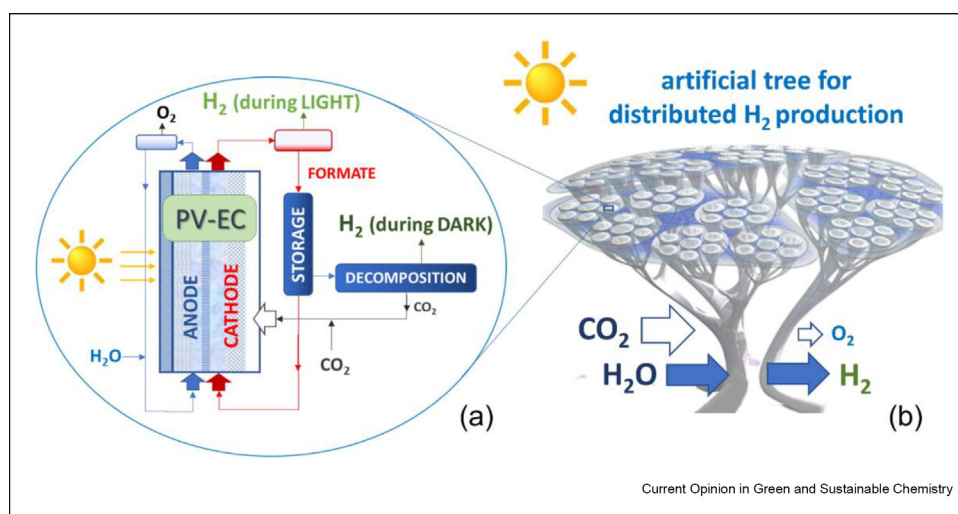
Figure 2 illustrates the conceptual view of an artificial tree for the decentralised production of H_2 that incorporates chemical H_2 storage as formic acid [29].

This AL technology is often considered to have only long-term use. However, their development is much faster than expected [29–31] and will be a key technology for the 4th industrial revolution (Industry 4.0) [32]. Companies such as ENGIE consider the development of AL as part of their adaptive strategy to maintain industrial leadership [33].

Electrification of the chemical industry

Electrification powered by low-carbon electricity supply, i.e. direct electric heating, is a preferred technological option in the near/medium term to meet the decarbonisation objective of chemical production [34,35]. The reason is that this solution offers a quick path to lower the carbon footprint, requiring minor adaptations in the process. However, due to large fluctuations in power production from renewables, processing plants need to be adapted to the availability of power from renewables. New plant design and engineering are necessary for flexibility [34]. Demand-response techniques must be developed to tune the plants to a variable supply dynamically. In addition, the new design in reactors to maximise effectiveness in electrical heating

Figure 2



Conceptual view of an artificial tree. Reprinted with permission from Ref. [29].

determines a change in heat transfer in several cases. The catalyst design has to be adapted. These are emerging areas but still need more attention [35,36].

A more advanced design is realised when the catalyst is directly heated by the Joule effect [36–38]. Other power-to-heat approaches include induction and microwave heating. However, an intrinsically higher thermal efficiency is possible by Joule heating. In addition, this design offers a series of creative possibilities for designing tailored temperature gradients in the reactor that optimise selectivity or even oscillating temperatures that provide new opportunities to improve performances or lower deactivation [39]. For example, the carbon footprint of CO₂ utilisation processes can be significantly reduced using a Joule-heated process combined with renewable electricity [40].

However, more efficient technologies where RE is used not simply to heat but as the direct energy source for the processes have to be developed [41]. The photo-, electro- and plasma-catalysis trio is the area on which research focuses. This is a fast-emerging research area and the basis for developing an e-chemistry, i.e., a chemical production overcoming the dependence on FFs. As an index of interest, 47 reviews dealing with CO₂ and electro, photo, and plasma keywords were published in 2023 (Scopus source). Nearly 3000 papers on these topics were issued in 2023.

Considerable attention is given in all these papers to mechanistic aspects and design criteria of the catalysts. However, it is emerging that despite the great effort, most of the studies are translating mechanistic approaches valid to thermal catalysis to electro-, photo- and plasma catalysis [42]. An effective catalyst design for this technological trio requires different fundamental approaches.

The current focus on the electrification paths in the chemical industry is on the synthesis component, e.g., the reactor and its role in contributing to GHG emissions. However, the reactor is only part of the chemical process. Taking as an example the steam cracking to produce olefins, e.g. a major source of CO₂ emissions (236 Mtons CO₂-eq. in 2019), only 23% of the total energy consumption is due to the heat of reaction (it is an endothermic process) [43]. 31% is related to separation, 22% to compression, and the remaining is lost. When discussing energy efficiency and comparing with new routes (making olefins from CO₂ via electrocatalysis, for example [3,44]), it is thus necessary to account for the efficiency in the whole process and how innovation in separation, particularly for decentralised (small-scale) production can drastically change the picture and impact for a low-carbon future.

Low-carbon H₂

Producing low-carbon (green) H₂ and its integration into current chemical processes to lower their carbon footprint is undoubtedly an emerging trend in green and sustainable chemistry [45]. However, decisions in this area are often more political than technologically driven. H₂ can play multiple roles as feedstock in many already existing applications (refinery, ammonia, etc.), as an energy carrier (with limits in its storage and long-distance transport), as fuels (but not ideal from this perspective compared to conventional fuels) and as a heat source.

Substituting H₂ from FFs with low-carbon (green) H₂ is the first major trend because over 100 Mtons of H₂ are already used in chemical and refinery production [45]. However, if electricity has to be taken from the grid, even up to 2030–2040, the carbon footprint of H₂ from electrolysis is higher than that of H₂ from methane steam reforming [24]. On the other hand, the cost of electrolyzers (around 1M€/MW) is too high for amortisation within a few hours (4–5 h) when only renewable electrical energy is available. It is thus not a valuable route, and alternative H₂ productions (less costly and lower carbon footprint than electrolysis with electricity from the grid) have to be developed [24]. Surprisingly, too little attention is still paid to these alternatives. However, it will soon become an emerging trend.

The other solution, also yet to be investigated, is to drastically decrease the fixed costs of electrolyzers, with a low cost as an objective rather than an efficiency. Low-cost electrolyzers thus require a change in the approach, but it is the only solution to developing solar-to-H₂ solutions. Figure 2 is an example of this change in the perspective with respect to current methods. In general, less efficient but much less costly electrolyzers that can be directly coupled with PV cells (e.g. operating without dependence on the grid) must be developed. The electrolyzers must be designed to work with low current densities and a discontinuous supply provided by PV.

Potential technologies that can produce direct (one-step) hydrogen carriers (such as ammonia) should be developed to exploit sunny regions, preferably with the valorisation of the anodic reaction of the electrolyzers (O₂ produced in water splitting has a minor commercial value). The availability of such types of hydrogen carriers at competitive costs could revolutionise chemical production. However, the current technologies (for example, in producing H₂ by electrolysis and then ammonia by Haber-Bosch process) cannot be effectively competitive for this objective.

Low-carbon H₂ routes will effectively impact the chemical industry only when the above aspects are

recognised on a larger scale, going beyond electrolyzers. However, there needs to be a consensus on this idea.

Conclusions

Analysing the emerging trends in green synthesis and sustainable processing routes requires going beyond the twelve principles of green chemistry. We have thus discussed this topic from the viewpoint of the leading emerging industrial directions and needs, as well as the future scenario.

Some trends could be identified: carbon neutrality and defossilization of the chemical industry, electrification of the processes and introduction of low-carbon H₂ routes. They are, in part, different faces for the same grand challenge, e.g., substituting fossil fuels as carbon and energy sources in chemical production, requiring a disruptive transformation in chemical production technologies. It requires passing from thermocatalytic processes (accounting for over 90% of the actual processes) to technologies using RE as the driving factor, e.g. photo-, electro- and plasma catalysis technologies [3]. These novel methods can be briefly indicated with the term e-chemistry [41].

This challenge requires discovering new catalysts and understanding how to use these novel technologies creatively, opening new possibilities and solutions [41]. At the same time, there is also the need to revise technology fundamentals. For example, passing from thermo-to electro-catalysis requires using novel concepts in their design and mechanistic interpretation [4]. Methodologies based on DFT to investigate surface mechanisms in thermo-catalysis reveal several limits in electro-catalysis, even if they are still the most used. Thus, alternative approaches, such as those based on localised phonons, must be used [42].

These novel technologies introduce the next steps in green synthesis and sustainable processing routes, e.g., what identifies artificial leaves/trees or sola-to-X technologies. They provide the technological bases for a distributed and resilient “green” chemical production using local resources and solar energy, e.g. not depending on the grid to supply electrical energy. This creates the technology basis for a new model of green communities integrating chemical and energy production to avoid dependence on externalities.

Although several scientific and technological advances are required to implement this disruptive direction, it is an emerging trend. We suggest that is the future for sustainable chemical production.

However, it is neither possible nor the scope to present a complete picture of such a broad and complex topic, as well as pros and cons. We identified trends,

opportunities, and personal concerns regarding some of the emerging directions and mainstreams, hoping to provide clues to analyse this complex topic rather than to present a state-of-the-art and discuss the offered examples in depth.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: G Centi reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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