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Status and gaps toward fossil-free sustainable chemical production†

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Chemical production needs to transform radically toward fossil-free sustainable chemical production to meet the targets for net-zero emissions by the year 2050. The feasibility of this transformation, the motivations, status and gaps, and perspectives are discussed after introducing how this change also implies a change in the model of production. Realizing the defossilization of chemical production involves electrifying the chemical processes, especially crucial elements such as chemical reactors, and the direct use of renewable energy to drive the chemical reaction. With a focus on electrocatalysis, the most relevant cases of (i) light olefin production, (ii) direct synthesis of main intermediates such as formaldehyde and acetic acid, and (iii) the production of aromatics are analyzed. The feasibility of these routes in the short–medium term is shown, while other cases such as the direct synthesis of ammonia from N_2 require turning the approach to other directions. On a global scale, defossilization of chemical production is feasible in the medium–long term with a cut of over 800 Mt per year CO_2 eq. emissions in line with the expectation to reach the net-zero emission target. A final section introduces a short discussion about some critical questions regarding the sustainability of fossil-free chemical production.

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Introduction

Chemical production is facing a major challenge in the next decades, due to a combination of factors:

- The pressure to phase out the dependence on fossil fuels (FFs) to reduce greenhouse gas (GHG) emissions and meet socio-political targets such as reaching Net Zero Emissions by the year 2050.

- The change in the nexus between energy and chemistry, which is largely related to the ongoing energy transition, and its impact on the availability and costs of raw materials for chemical production.

- 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 several elements of petrochemical production.

- The geopolitical pressure to overcome the limitations related to the large monopoly of FF production and distribution.

Cetinkaya *et al.*[1] of McKinsey & Co. (a major consulting company) some years ago warned petrochemistry that "the old models for value creation are losing traction and that the advantaged-feedstock-opportunity window is closing", indicating the need to change the model of development.

Drivers to develop a new model of chemical production

We could identify two main driving factors in the current model of petrochemical production:[2] the use of FFs and the scale economy. These are two interlinked components of the model of development because over 90% of the raw materials for chemical production are based on FFs, but less than 40% on average is used as carbon sources or to increase the energy value of the product (the ratio of the output energy potential useful – exergy – to the potential exergy input for chemical production is around 30%).[3]

Most of the FFs used in petrochemistry are needed to produce the heat and the energy used in the chemical processes. In addition, most of the chemicals are not produced directly, but involve an often-complex sequence of processes, thus with a progressive loss of energy efficiency (in the global process). Chemical production is strongly linked to the combustion of FFs used to produce the heat and energy necessary to run the chemical transformation and separation. Heat recovery is thus a critical element to achieve acceptable overall energy efficiency, and from here the motivation to have a scale economy, *e.g.*, large plants integrated into complex chemical/

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†This manuscript summarizes the concepts and discussion that emerged from the large EU initiative SUNERGY (fossil-free fuels and chemicals for a climate-neutral Europe; **https://www.sunergy-initiative.eu**).

refinery sites. Heat recovery is efficient only in large-scale plants.

This model of chemical production is now suffering from significant limitations, from the large environmental impact to the low circularity and integration with local resources. Especially critical now is the low capacity to adapt to a changing world where flexibility in production, time to market and the possibility of accessing a wider range of investors are the keywords for success. Transformation of chemical production is thus motivated not only by the need to reduce the carbon footprint, but also derives from several interlinked social, economic and industrial factors. The result is a push to develop new models of chemical production, generating new windows of opportunity overcoming the strong hierarchical structure of current chemical production: oil refinery, then production of chemical raw materials, then base and intermediate chemicals, *etc*. Distributed chemical manufacturing, modularity and scale-up of chemical processes by numbering are among the emerging elements of a novel model of chemical production,[4–7] requiring new technologies largely based on the new opportunities offered by renewable energy sources (RES) and process intensification.[8]

Developing FF-free chemical production is thus an opportunity to create new models of growth and economic development, value chains and innovation, and not only a target to reduce GHG emissions.

The new model of fossil-free sustainable chemical production

There are different opinions on whether phasing-out FFs from chemical production is feasible from an economic perspective, or even needed. In addition, quite a spread of opinions exists on timing; for example, whether substituting the use of FFs will be a key element to meet 2050 net-zero emissions targets, or whether instead it will occur in an even longer-term perspective.

More detailed discussion of these aspects could defocus this perspective. Some further considerations and supporting data for the discussion were earlier reported.[9–11] Here we limit the analysis to the status, gaps and limits of the developments in the area to provide suggestions for this debate from a technical and socio-economic perspective. In addition, the aim is to offer a different, vision-oriented analysis of the opportunities for research in this area, rather than to debate in detail the pros/cons of substituting FF use in chemical production.

We call this novel chemical production alternative to the current petro-chemistry '*e*-chemistry'.[12] We assume a high-tech scenario of transformation of chemical production, driven by the forces and motivations indicated before. This high-tech scenario requires an intense R&D effort to develop the new routes necessary to substitute the use of FFs in chemical production, with the energy largely provided by renewable sources, if not directly from solar light, and the use of alternative carbon sources to FFs.

This high-tech scenario considers that a significant part of the chemical products will be transformed in this direction before 2050. From around the years 2030–35, it is expected that new plants based on the old petro-chemical routes will not be introduced. These are assumptions based on the realization of this high-tech scenario, which is difficult to prove, especially regarding the timing. However, even if this scenario

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is realized later, it is still necessary to consider and prepare the technologies, catalysts, *etc*. for this transformation. There are already various indications that this transformation has irreversibly started.

Alternatives in transforming chemical production

The chemical and refinery industry is already showing signs of recognition of the change in the value chain and nexus between refinery and chemical production,[13] because of the loss of economic value in producing liquid fuels in refineries. One of the signs is the increasing attention given to the so-called *crude oil-to-chemicals* (COTC) processes.[14–16] This term indicates the direct conversion of crude oil to high-value chemical products (olefins, in particular) rather than producing them from refinery side streams. The industrial effort in this direction is a clear sign that the energy–chemistry nexus and the refinery–chemical production value chain are transforming.

Several COTC projects (announced or started) plan the reconfiguration of refineries to enhance the production of chemicals (>40% per barrel of oil to chemicals, rather than <10% as in a conventional refinery).[15,16] Among the strategies explored in COTC plants are (i) direct processing of crude oil in steam cracking, (ii) integrated hydro-processing/de-asphalting and steam cracking and (iii) processing of middle distillates and residues using hydrocracking technology.

These projects aim to preserve the use of FFs as the backbone of chemical production, refocusing the refinery production on higher added-value products. Thus, the production of raw materials for petrochemistry is directly integrated into the refinery scheme. The impact of COTC in meeting low or zero-carbon targets is negligible, or only indirect (COTC plants will decrease the production of transport fuels). In addition, adapting the refineries to the production of raw materials for petrochemistry will increase further the size of the actual steam crackers (the most used technology to produce olefins, with plants having an average size of 500 kt per year) by a factor of 4–10. The consequence is a further lowering of the capability to adapt to current market dynamics, the long-distance transport of chemicals and the environmental/safety impact, *etc*; in other words, the opposite of what is required to transform chemical production into a more sustainable model. Thus, the COTC solution, although actively considered by refineries, does not appear to be the necessary strategy to move to fossil-free sustainable chemical production, but rather is a short-term strategy to continue to preserve the dominant role of FFs in chemical production.

Another general objection to moving to FF-free chemical production is that a reduction of the carbon footprint could be achieved by substituting the use of FFs as the source of heat/energy (electrification of furnaces, *etc*.) while still maintaining hydrocarbons as the preferable carbon source for chemical production. The use of FFs preserves the linear model of the use of carbon, from the extraction of FFs to the production of waste and CO_2 as the final products.[9] A sustainable model of production must have as a target the closure of the C-cycle (circular carbon use), by increasing the use of waste/CO_2 as a carbon source, integrated eventually with the use of low-carbon footprint raw materials (biomass).

Thus, the motivations for substituting the use of FFs as a carbon source in chemical production are to enhance sustainability, realize the integration with local resources, and application of a different model of production with reduced dependence on external resources that have a high monopoly character, *etc*. This does not necessarily correspond to higher costs but to a different window of opportunities, which is a direct consequence of the change in future societal and industrial models of development.

Looking to FF-free sustainable chemical production is thus not an academic exercise, but an effective, industrially relevant direction to explore for a new model of chemical production.

Scope and limits

This perspective aims to provide a holistic analysis of the transformation to fossil-free chemical production which is not present in the literature. It is thus organized into a first part in which the socio-economic motivations are analysed, because often a comprehensive analysis of these elements is missing, even though the discussion is limited to the main elements and depends on the scenario assumed.

The second part analyses the feasibility of implementing a high degree of substitution in the use of FFs for chemical production, and the key technologies, and their status/gaps, to realize this challenge. Transforming chemical production toward a fossil-free model is a deep transition, requiring a simultaneous and synergic convergence of the various technologies necessary. For this reason, the focus here is to provide this general analysis, rather than to discuss each technology in depth, which would defocus the discussion. At the same time, some of the aspects that need to be better understood to implement the technologies under development are highlighted.

The third part then attempts to analyse the impact in terms of reduction of GHG associated with the transformation to fossil-free chemical production, with the fourth and final part dedicated to analysing some of the questions about the sustainability of this transformation.

To focus this manuscript, the discussion here is limited to technologies that have direct use of renewable energy (RE) and alternative carbon sources to FFs. Power-to-X (PtX) technologies, where the only step of direct use of RE is the production of H_2, by electrolysis, are not analysed here. These technologies have been developed at already relatively high TRL (technology readiness levels) and are discussed elsewhere.[17–21] They suffer, in general, from high costs and ongoing issues in coupling the different steps (electrolysis followed by one or more downstream thermocatalytic steps). Direct technologies to the final products, for example, the direct electrocatalytic conversion of CO_2 and H_2O to methanol or ethylene, offer potential advantages in terms of energy efficiency, process intensification and cost reduction, although their development is still challenging.[22]

To demonstrate the need for direct electrocatalytic production technologies, the exergy loss by comparing the direct *versus* multistep processes in olefin production could be analysed.[23] For future low-carbon production, exergy analysis offers a better, integrated evaluation tool to consider the energy and material efficiency of a process.[24] We can compare two solutions, both based on the production of light olefins from CO_2, H_2O and renewable energy. The first route A is based on technology already at an advanced stage of development, based on the production of H_2 by electrolysis, then thermocatalytic conversion of CO_2 + H_2 to methanol, and a further stage of methanol-to-olefin (MTO) conversion. The exergy loss, in this case, is about 50%, *i.e.*, about half of the exergy (the capacity of energy to do physical work) is lost in the transformation. If biomass is used *via* gasification and methanol synthesis, the exergy loss is even higher (around 70%),[25] while slightly below 50% for waste to olefins *via* methanol synthesis and for the conventional steam cracking process.[23] Even for an advanced electrocatalytic process, like the co-electrolysis at high temperature of CO_2 and H_2O to directly produce syngas followed by methanol/MTO processes step,[25] the exergy loss is about 50%. This can be estimated by combining the data on the exergy of methanol production *via* syngas (by co-electrolysis)[26] with the data on the exergy of the MTO. In a direct CO_2 to olefin electrocatalytic transformation, an energy efficiency above 70% could be a feasible target. Thus, developing a low-carbon chemical production alternative to current petrochemistry would always require considering direct electrocatalytic processes, when possible, even if challenging.

It should be pointed out that in the MTO process a range of hydrocarbons is produced, requiring complex separation procedures as outlined in Fig. 1a. In the case of the direct electrocatalytic conversion of CO_2 and H_2O (Fig. 1b), a simplified procedure of separation is possible thanks to the higher selectivity of the process. Following the scheme proposed by Pérez-Ramírez and coworkers,[27] a sequence of three PSA (pressure swing absorption) units may allow the separation, with recycling of CO_2, H_2O and eventually H_2 in the case of a pressurized electrocatalytic unit. As visually emerges from the comparison of these two routes, route B of direct electrocatalytic conversion, concerning the multistep process involving electrolytic production of H_2 followed by a sequence of thermocatalytic steps, requires fewer steps, with thus a potential reduction of fixed and operative costs, in addition to the potential higher exergy efficiency.

The potential benefits in intensified processes (route B *versus* route A) are maximized in distributed chemical production models, *e.g.*, when small–medium-scale bio/solar refineries well integrated with the use of local resources will supply the needs of materials and other chemicals for the territory.[28,29] The current model of chemical production is based on applying scaling laws in process engineering, pushing to realize larger-scale productions which do not account for factors like environmental impact, transport costs, the capability of adapting to a highly variable demand and cost in raw materials, *etc*. These factors are currently pushing the need to change the production model toward distributed chemical production. In distributed production models, a

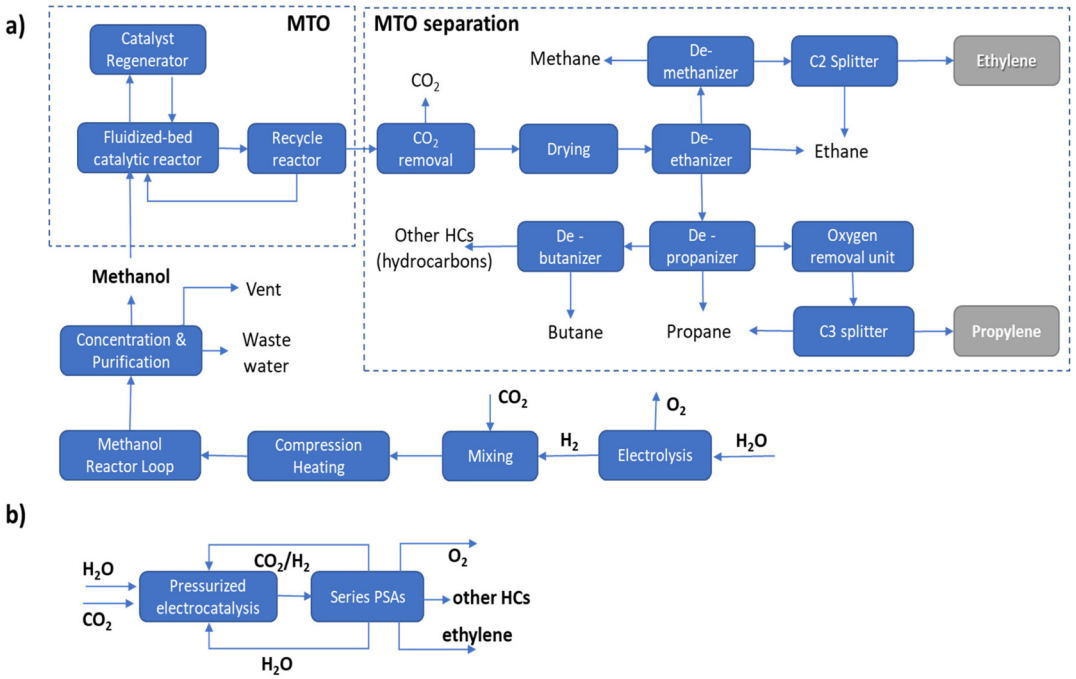

Fig. 1 Simplified block scheme of the process to synthesize olefins from CO_2: (a) route A *via* producing H_2 by electrolysis followed by thermocatalytic synthesis of methanol then converted to olefins by MTO process; (b) route B of direct production of ethylene by electrocatalytic conversion of CO_2 and H_2O.

requirement is a change of the technology, because intensified and highly adaptable technologies would be required.[8] Direct electrification of chemical production offers advantages in this sense over conventional thermocatalytic processes.

Many aspects contribute to determining the industrial feasibility, as reviewed recently by Mbatha *et al.*[30] for the power-to-methanol case. Among them, the availability of the technology at sufficiently high TRL is crucial. However, when considering the future of chemical production from a fossil-free sustainable perspective, the question is not only which technologies will be ready in the short term, but which technologies should be pushed to realize future production. For this reason, we focus discussion here mainly on direct electrification routes.

While other papers have reviewed the state-of-the-art of some of the topics addressed later, an analysis integrated into a framework assessment of this FF-free chemical production is generally missing. Furthermore, rather than focus on reviewing the scientific results with the identification of some design criteria to improve the performances (the scope of most of the reviews in the sector), the aim here is to analyse the technical feasibility, or identify gaps and limits, for the application as a novel sustainable production route to be part of a distributed chemical production model based on the use of local RES and carbon sources.

In addition, for the motivations explained above, we do not consider here technologies to produce CO from CO_2, being necessary then the further thermocatalytic upgrading to convert CO with H_2, the latter also produced separately by electrolysis or together with CO in co-electrolysis SOEC (solid oxide electrolyzer cell) technology.[31–35] Many researchers believe that this is the preferable route, in particular, syngas by co-electrolysis followed by thermocatalytic syngas conversion. We consider instead that investing in the development of this path as a preferential route to produce the raw materials for the future low-carbon chemistry may result in a slow-down of the transformation to a future fossil-free sustainable chemical production. This is a matter for discussion, and clear demonstrations of support for one or the other position are lacking. However, considering the investments which are needed, and the amortization time necessary (typically two decades), investing in intermediate technologies may result in a delay in the whole transformation process, rather than realising a step-by-step renovation. Although challenging, the process intensification possible by direct synthesis using RE should be the target,[8,36] even if the multistep routes *via* syngas production (for example, by co-electrolysis) is a more mature technology. We thus limit the discussion here to this scenario, but with the remark that its realization would require intensifying the research effort, and industrial convergence on it.

Defossilizing chemical production

The recent report of the International Energy Agency (IEA) on the role of chemical production to meet the NZE target[37] showed that direct CO_2 emissions from primary chemical production were 920 Mt CO_2 in 2020, the third largest industry subsector in terms of direct CO_2 emissions, behind cement and iron and steel. However, it is expected that it will be difficult for these two industrial sectors to reduce emissions to meet the target of Net Zero Emissions by 2050 scenario. Chemical production should instead achieve the NZE target even before 2050 according to the IEA scenario. Thus an even higher rate of decrease in greenhouse gas emissions is required for the chemical sector than the average for the industrial sector. If the actual trend in the reduction is extrapolated to 2050 (see Fig. 2), only around half of the target reduction necessary to arrive at NZE by 2050 will be achieved. Defossilization of chemical production thus requires (i) to more than triple the average yearly rate of CO_2 reduction with reference to what was made in the last decade,[38] and (ii) have a rate of decrease for the chemical sector even higher than that of other industrial sectors. Thus, these are challenging objectives.

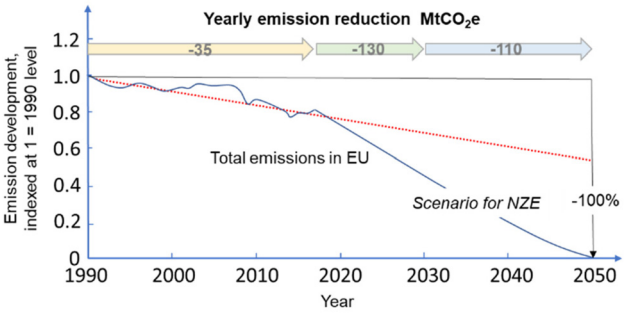

Fig. 2 Trend in total emissions in EU (indexed at 1 = 1990) and predicted trend to meet the NZE scenario. Based on indications in ref. 38.

Direct CO_2 emissions in the production of chemicals derive both from energy and process emissions. Around half of the chemical energy input is consumed as feedstock, *i.e.*, fuel used as raw material input rather than as a source of energy. If the process emissions are also added, between 30–40% of the inlet carbon as FF is retained in the final chemicals/materials (even less in some cases), while the remainder is used for the transformation and is emitted as CO_2.

Even the part of the carbon stored in the chemicals/materials (the final products of the chemical transformation) at the end of the life result in further emissions. The average non-biogenic content of municipal solid wastes (MSW) is typically around 40–50%, thus resulting in additional CO_2 emissions, for example when these wastes are sent to incineration. Furthermore, additional chemicals and materials are released into the environment and are not part of MSW.

Thus, together with the electrification of unit operations (especially chemical reactors) in industrial plants to reduce the use of FFs as an energy source for the operation of these units, it is also necessary to substitute FFs as the carbon source for the chemical industry to meet the requirements for NZE targets. The strategies to achieve emissions targets of the chemical industry should thus include:

(i) Phasing out non-renewable energy resources,

(ii) Fostering a transition to a circular economy and the use of green electricity, and

(iii) Electrifying heating and industrial processes.[39–41]

Primary chemicals include ethylene, propylene, benzene, toluene, mixed xylenes, ammonia and methanol. Their production accounts for two-thirds of energy consumption in the chemical and petrochemical sector. An analysis of the possibilities and scenario toward a fossil-free sustainable chemical production could thus start from the analysis of how to realize the defossilization of these primary chemicals. As these chemicals are also largely the input for many intermediate and final chemicals,[2] focusing attention on them implies a cascade effect on industrial chemical production as a whole.

We will start with the analysis of the electrification of the chemical processes, with a focus on reactors.

Electrification of the chemical processes and reactors

Electrification of the chemical processes involves a broad range of options. The objective is to substitute with green electricity operations currently involving FFs, thus mainly those related to furnaces (accounting for about half of the current emissions of CO_2 in energy-intensive industries),[42] but also those associated with the production of steam, hot water, and space cooling/heating.

An estimation of the electrification potential in the EU for the chemical sector is reported in Table 1.[43] The electricity demand can be divided into two aspects: that necessary to supply heating or cooling (indicated as electricity thermal), and that used in mechanical power and lighting, indicated as electricity other. The energy from combustible fuels can be separated by considering the temperature range of use. In general, about one-third of the energy input is lost due to inefficiencies and energy losses within the plant.

Power-to-heat is a term often used to indicate these technologies. They include the use of various electromagnetic (*e.g.*, induction, magnetic, microwave, plasma) and heat pump technologies to substitute those actually in use, mainly related to heat exchangers and FF combustion. Electromagnetic heating offers in general a more precise control of the temperature, faster response, and in some cases also the possibility to induce rapid modulations in the temperature, and a broader turndown across a range of operating conditions. However, most of these technologies are still at the laboratory or pilot scale. The deployment will also require more efficient power sources and modular platforms.[41]

Electricity can also provide the driving force for pressure-driven membrane separation processes or the production of H_2 by electrolysis of water.[44] Hydrogen can be then used for high-temperature heating. Note that in moving to distributed models of production, the use of power-to-heat technologies offers the additional advantage of process intensification, which is a requirement for small-scale production. In addition, heat integration is typically less efficient in small-scale processes, where high flexibility in production is another requirement. These aspects have to be accounted for when adding further benefits in the introduction of power-to-heat technologies for distributed, small-size chemical production plants.

Table 1 Energy demand in the European chemical industry and alternative electrification options. Elaborated from the data in ref 43.

Energy service	End-use	Share, %	Electrification technology
Other	- General appliances & machinery	13	
Thermal	- Space heating - Process cooling	9	
< 100 °C	- Space heating	6	- Electric boilers - Compression heat pumps
	- Thermal cooling		- Microwave and infrared dryers
	- Thermal drying		- Compression chillers - Thermoelectric cooling
100–400 °C	- Steam - Polymers manufacture (*e.g.* extruders, melters)	59	- Electric boilers - MVR - Microwave and infrared dryers - Electric reactors
400–1000 °C	- Crackers & reformers (fuels only) - Superheaters - Limekilns	13	- Electric crackers and reformers - Electric boilers - Electric calciners

Heat pumps are an alternative to traditional steam or oil heating. By using novel fluids (liquid CO_2, for example), heat pumps can be adapted to lower and higher temperature ranges than the current ones. However, especially for high-temperature operations, costs and stability are still issues. Electromagnetic heating offers novel possibilities for optimizing reactor and furnace design, in addition to a drastic cut in CO_2 emissions (possible only when green electricity is available in the amount and with the continuity necessary for chemical processes operations) and process intensification.

Different possibilities for heating reactors using electricity exist. Fig. 3 illustrates schematically the different options possible concerning the case currently most used of (catalytic) chemical reactors where the energy is provided (directly, indirectly) by FF combustion. For temperatures below about 550 °C, an external fluid is typically used to transfer the energy. A temperature gradient is present with respect to the walls of the reactor element where the reaction occurs (in a fixed-bed reactor, a tube of about 3 cm diameter where the catalyst in the form of pellets is contained – see Fig. 3.1b for a case of an endothermic reaction). The fluid external to this tube where the reaction occurs is then externally processed in a furnace (as in Fig. 3.1b, or an, analogous system when cooling could be necessary; eventually a further intermediate exchanging fluid, such as high-pressure steam could be used). When reaction temperatures higher than about 550 °C are necessary, the direct firing of the reaction tubes is necessary, as in crackers or reformers. Thermal transfer is less efficient in these cases and thus more accentuated temperature gradients are present (see Fig. 3.1a). The process is typically limited by

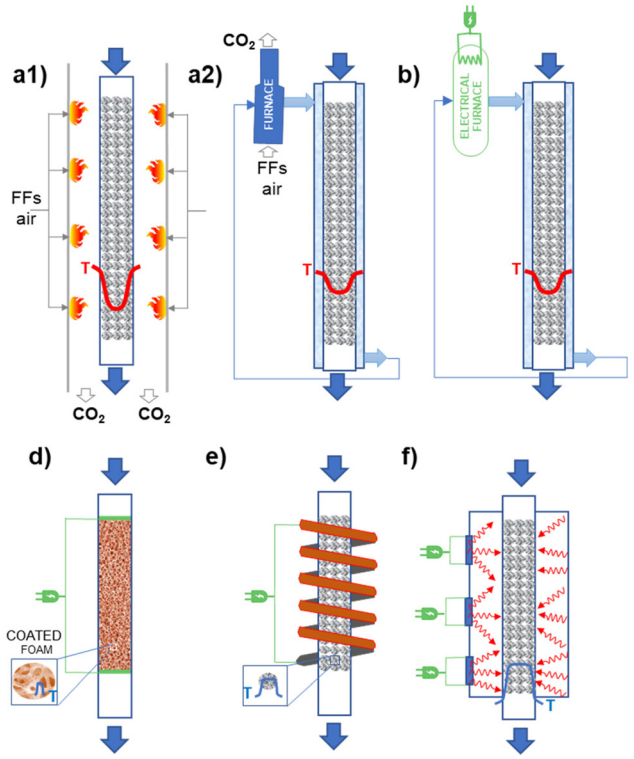

Fig. 3 Schematic illustration of catalytic fixed-bed reactors where the energy for the process is provided directly or indirectly by FFs combustion (a1 and a2, respectively) and the alternative possible for electrification: (b) electrical furnaces/boilers, (c) ohmic or Joule effect (a metallic foam), coated with a catalyst layer, directly heated by an electrical current, (d) magnetic inductive heating (for core–shell catalysts pellet, where the core is a magnetic nanoparticle) and (e) microwave/RF heating of a fixed-bed catalyst bed. The temperature profile in the reactors is also schematically presented.

thermal transfer. The possible options to electrify the catalytic reactors are summarized below:

1. *Electrical furnaces/boilers*: when a heat-transferring fluid is present, an electric boiler could be simply used (Fig. 3.2). This is the simple electrically heated reactor, easy to retrofit and already at a high TRL, but essentially not influencing the mechanisms and limits in heat transfer. Thus, this does not offer opportunities for process optimization.

2. *Ohmic or Joule effect (inductive heating)*: electrical resistances are inserted directly in a body (like monolithic support, on which the catalyst is then washcoated) present in the catalytic bed of the reactor. An alternative is that the electric current passes through a resistive conductor, such as metallic support, on which the catalyst is deposited. The catalyst is in direct contact with the electrically heated surface resulting in better heat transfer mechanisms. It is also possible to heat at the temperature necessary for the catalyst layer while maintaining at a lower temperature the fluid in contact with the catalyst. Thus, selectivity or stability could be improved. The catalyst must be designed specifically for operations in this reactor (for example as a thin coating). As for cons, a specific redesign for intimate contact between the electric heat source and the catalyst is necessary. It is also necessary to avoid the possibility that a heated surface enhances side reactions.

3. *Magnetic heating*: a rapidly alternating magnetic field either generates eddy currents in conducting materials resulting in the Joule heating of those materials, or generates heat in ferromagnetic materials by magnetic hysteresis losses. As reported in the literature from the long term, and used industrially in some cases, it remains a challenge for wider industrial use. The core–shell (or analogous) design has to be realized, with a core of components which is heated magnetically. Often these magnetic nanoparticles can be also catalytically active in side reactions, and their direct contact with reactants should be avoided. It is possible to realize fast changes, and also periodic fast modulations in the temperature. Very localized heating at the catalyst, with the possible creation of thermal gradients with a flowing gas phase (rapid quench), is possible.

4. *Microwave/RF (radio frequency) heating*: are both volumetric heating methods; the rapidly alternating electric field of the microwave generates heat by moving dipolar molecules or ions in liquids, or by getting absorbed in the so-called "dielectric lossy" solid nonmagnetic materials. There is industrial experience, especially in the area of synthesis of fine chemicals. As for cons, the approach is effective with liquids, but less so with gas reactions. The main challenge with heterogeneous catalysts is to achieve uniform heating, in pilot as well as industrial-size reactors. Furthermore, the proposed solutions are difficult to scale up.

Except for the first case, a general redesign of both the catalysts and reactor geometry and characteristics is necessary to take full advantage of electrification. Thus, substituting the use of FFs with electrical energy as supply also becomes an opportunity for innovation and improvement in performance. On the other hand, scale-up of these solutions, except the first, remains challenging, with a technology maturity which can be indicated at a TRL value between 3 and 5.

Among the important challenges, the possibility of realizing spatial and temporal control of electricity-generated thermal fields also requires the design and fabrication of energy-responsive catalysts.[8] Controlling and optimizing the overall energy efficiency is another necessary objective, which involves a better-combined understanding from a multidisciplinary perspective of the underlying phenomena.

Studies in the literature on electrically heated reactors are still limited. One of the first studies was that presented together by Haldor Topsoe and DTU[45] (Denmark) for a steam-methane-reforming (SMR) reactor for hydrogen production. By closely integrating the electric heat source and the catalysts it is possible to increase catalyst utilization and limit unwanted byproduct formation. The process intensification is of a factor of around 100. Fig. 4 illustrates the reactor concept and the profile of temperature present in the electrical reactor based on direct resistive (ohmic) heating.

The authors tested the concept in a laboratory-scale reactor based on a FeCrAl-alloy tube, which is the resistive heating element, chosen for having the electrical resistance indepen-

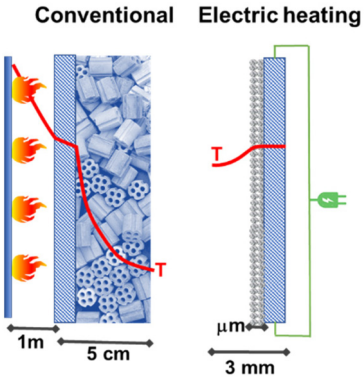

Fig. 4 Conventional fired reactor *versus* electric resistance-heated reactor with an indication of the radial temperature profiles. Adapted from ref. 45 with permission. Copyright © 2019, The American Association for the Advancement of Science.

dent of the temperature in the range of interest. This tube (around 6 mm diameter, length about 0.5 m) was inner-coated with a nickel-impregnated washcoat of about 130 microns.[45,46] This reactor allows around 90% conversion to syngas with a feed of about 1.7 L min^{-1}. The AC current was applied to copper sockets mounted at opposite ends of the external surface of the reactor tube. The tube was then inserted into high-temperature insulation material. The authors indicate that this reactor is scalable to industrial conditions and capacities. However, for a typical industrial reformer (50.000 m^3 h^{-1}), around 500,000 of these (lab-size) reactors should operate in parallel. Even considering the use of this technology for small-scale distributed production of H_2, the problem of providing the renewable energy necessary for operating in parallel a large number of reaction tubes still represents a major challenge.

Ghent University (Belgium) has reported a recent assessment, mainly based on ex-ante LCA analysis, of electrified processes for methanol production: (i) plasma-assisted and (ii) electrically heated thermocatalytic dry methane reforming.[47] The first path has lower greenhouse gas (GHG) emissions only when the plasma reactor is powered by renewable electricity. However, both routes have a low climate change impact (around 0.6–0.7 kg CO_2-eq. per kg_{MeOH}) when all the process units are electrified by renewable electricity. Similar results were obtained for CO_2-based methanol production utilizing electrolytic H_2. Over 40% CO_2 emission reduction is possible by these electrified routes with respect to conventional, state-of-the-art, natural gas steam reforming-based methanol process. However, the availability of fully renewable electricity for continuous operations is required.

Politecnico of Milano's (Italy) group has recently made a numerical assessment of electrically heated (Joule) methane steam reforming over structured catalysts.[48] The structured catalysts are used as internal heating elements. They suggest that SiC is the preferred material to be used as catalyst support since the currents and voltages to be used can be safely employed. Differently, metallic materials require higher current densities and applications at very low voltages. The reactor models consider two types of structured catalysts: (i) open-cell foams and (ii) honeycombs, both coated with an Rh-based catalyst. The first, however, was indicated as preferable.

Palma and coworkers[49] and Rieks *et al.*[50] also studied the steam reforming and dry reforming of methane, respectively, using a commercial electric heating element in silicon carbide coated with a thin layer of nickel catalyst. However, the geometry of these materials was not optimized for efficient radiative heat transfer. The geometry of these systems must allow a large area for the catalyst and avoid significant bypass.

Catalysts should be also specifically designed to take advantage of the possibilities given by electrified chemical reactors. However, studies are still quite limited. Wismann *et al.*[51,52] showed that by using alumina-supported $Co_xNi_{(100-x)}$ nanoparticles with defined alloy compositions, the induction heating for steam methane reforming may be tuned. The approximately 30 nm Co–Ni particles were identified as optimal for operating both as a catalyst and as an induction heating susceptor.

Pham-Huu, Giambastiani and coworkers[53] have analysed the opportunities offered by electromagnetic induction heating technology to improve catalytic heterogeneous processes. The possibility to overcome heat transfer limitations and associated effects, such as slow heating/cooling rates, non-uniform heating environments, and low energy efficiency, particularly in strong endo- and exothermic catalytic reactions, was evidenced. The use of microwave (MW)-assisted heterogeneous catalysis was reviewed recently by Muley *et al.*[54] Microwave heating applications ranging from methane conversion to ammonia production, biomass conversion, *etc*. were discussed. Vlachos and coworkers[55] reviewed very recently the advantages and possibilities offered by MW heating for multiphase reactors. The use of MW in combination with heterogeneous catalysts was also recently reviewed by Palma *et al.*[56] They also discussed the mechanistic effects and energy losses, as well as the problems associated with scale-up. A recent paper discussing how to pass from the bench to pilot scale in MW-driven structured reactors for methane dehydroaromatization was published by Santamaria and coworkers.[57]

An example of process intensification by electro-magnetic induction heating for water catalytic treatment was reported by Munoz *et al.*[58] Yassine *et al.*[59] used the possibility of spatial resolution in temperature at the micro-level offered by induction heating of magnetic nanoparticles for the conversion of resazurin into the fluorescent resorufin, in solution and when confined in small hydrogels, to prove this concept. Chaudret and coworkers[60] developed iron-carbide nanoparticles as promoters for magnetic heating of nickel-based catalysts for CO_2 hydrogenation. The same goup[61] also reported the optimization of the reactor and Ni/CeO_2 catalyst (by adding iron nanoparticles) for magnetic CO_2 methanation.

Much attention to this topic is also given by industry. For example, BASF, SABIC and Linde have signed a joint agreement to develop and demonstrate solutions for electrically

heated steam cracker furnaces. The interest of Haldor Topsoe was indicated previously. Many internal projects are underway by major chemical companies.

Direct electrification of the catalytic reactions

The area often generically indicated as power-to-chemicals lumps together processes where the renewable energy directly provides the energy necessary for the reaction, in the form of either activated reactants (as in plasma-catalysed processes)[62] or of species generated on the surface of the catalyst by application of potential, *i.e.*, electrocatalysis.[37] Light adsorption on semiconductors also generates a charge separation and thus reactive species, overcoming (in principle) the need to provide externally the energy (heat) to overcome the activation barrier.

However, there are some differences in photoactivated processes concerning the electrocatalytic processes: (i) the catalytic surface must be directly irradiated by solar light, and thus process intensifications (such as those possible by using stacked electrocatalytic reactors) are difficult to realize; (ii) the current density generated by light adsorption is typically low, of the order of 10 A cm^{-2}, and thus productivity is low; in electrocatalytic processes, the current density can be up to two orders of magnitude higher; (iii) while different sources of green electricity could be used, direct solar-driven processes are highly dependent on irradiation intensity, thus depend on meteorological aspects, localization, *etc*.

Although direct photodriven processes have other advantages, the issues to solve before commercialization, except perhaps in a few cases (such as H_2 photo- or photoelectro-catalytic production),[63] are more severe with respect to electrocatalysis. To restrict the discussion, only electrocatalytic and plasma-catalysis are considered here. For analogous reasons, concentrated solar panel (CSP) technologies are not considered in the power-to-heat section.

In addition to generating an alternative path providing the energy necessary to overcome the activation barriers, direct electrification paths can also generate *in situ* the other reactants needed to make the catalytic reaction, for example, the H^+/e^- equivalent of H_2 for hydrogenation reactions. Less studied, but also active oxygen species, including peroxo ones, could be generated *in situ* for direct or mediated oxidation reactions. Thus, electrification also offers the advantage of eliminating the need to separately produce these redox reagents. This could result in a novel process offering potential cost reduction, improved efficiency and reduced GHG emissions.

Electrochemical non-oxidative deprotonation to light olefins. An example of this type was presented recently by Wu *et al.*[64,65] reporting a new process (called LoTempLene) to produce ethylene from ethane. The core concept is the use of electrochemical non-oxidative ethane dehydrogenation using solid-oxide membrane reactors/stacks. Ethane is fed to the anode where it is deprotonated to produce ethylene and protons, the latter passing through the solid membrane to the cathode where they recombine with electrons to produce hydrogen. Fig. 5 presents the schematic drawing of the electrocatalytic cell, with an SEM (scanning electron microscopy) image of the electrodes/membrane assembly.

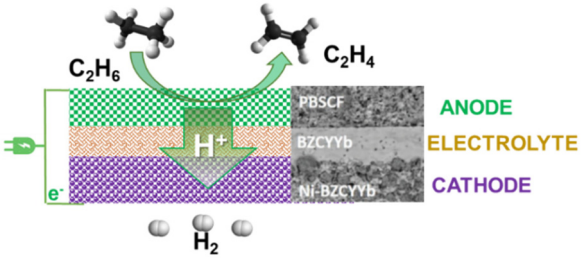

Fig. 5 Schematic illustration of the ethane to ethylene + H_2 coproduction on solid proton-conductive membranes in an electrochemical cell. Adapted from ref. 65 with permission. PBSCF = $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (porous double perovskite, 30 μm). BZVYYb = $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (doped barium zirconate cerate, 10 μm). Ni-BZCYYb = NiO : BZCYYb 6 : 4 wt. Copyright © 2018, Royal Society of Chemistry.

This consists of a dense 10 mm-thick BZCYYb electrolyte thin film on porous BZCYYb-Ni anode support (300 mm) and a porous double perovskite $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) layer (30 mm) as a cathode. BZCYYb is a barium zirconate cerate ($BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$), a low-temperature ionic conductive solid electrolyte. At 400 °C (thus about 200–250 °C lower temperatures than for the catalytic ethane dehydrogenation), a current density of 1 A cm^{-2}, corresponding to an H_2 production rate of 0.448 mol cm^{-2} per day (about 0.4 L h^{-1} cm^{-2}), near 100% ethylene selectivity could be achieved under a low electrochemical overpotential of 140 mV (thus high energy efficiencies). This approach can save about 65% in the process energy and reduce the carbon footprint by over 70% compared with an industrial ethane steam cracker. Scalability and stability still have to be demonstrated. However, the concept of direct electro-assisted dehydrogenation opens new possibilities in chemical processes. By using low-temperature proton-membranes, and suitable electrocatalysts, many valuable alternative chemical processes could be developed.

The concept is not novel. Wang *et al.*[66] about 15 years ago used a similar yttrium-doped barium cerate electrolyte, but for ethane fuel cells. A similar yttrium-doped barium cerate was used by Shi *et al.*[67] also over a decade ago for the co-production of power and ethylene by dehydrogenation of ethane. Power densities, however, were lower than those of Wu *et al.*[65] Various other papers and patents were also published later. Propane could be also efficiently dehydrogenated to propylene, with selectivities up to 80% but decreasing to 50% on increasing current density up to 80 mA cm^{-2}.[68] Thus, the approach is not new, but recent results raised the performances to interesting conditions for exploitation and linked specifically to the electrification of the production.

Direct electrocatalytic CO_2 to light olefins. More challenging concerning alkanes to alkenes conversion, and potentially more impacting in terms of GHG reduction, is the possibility of developing a new route to produce light olefins, one of the crucial base materials for defossilization of chemical pro-

duction and carbon circularity. Not surprising is thus the large recent interest in the electrocatalytic conversion of CO_2 to ethylene or propylene.

Various recent reviews have specifically discussed this reaction.[69–80] The focus of these reviews, however, was mainly on the mechanistic aspects triggering the C–C bond formation and selectivity to ethylene, or C2 oxygenates (such as ethanol). Features analysed included designing the electrocatalysts and the influence of the reaction conditions, with connected aspects such as how the pH at the electrode surface determines the performance and formation of ethylene or other products. Fewer studies were instead centred on the identification of the industrial feasibility of this approach. One of them is by Jaramillo and Sargent's group,[81] who undertook a techno-economic and carbon emissions assessment of CO_2 to ethylene (or other products) electrocatalytic production from the perspective of practical application. They indicated that to become competitive on this path with FF-derived feedstocks, electrical-to-chemical conversion efficiencies need to reach at least 60–65%, and renewable electricity prices need to fall below 2–4 cents per kilowatt per hour.

To produce 1 kg ethylene (C_2H_4), 0.428 kg H_2eq. generated by water electrolysis are required to form the $12H^+$ per mole ethylene necessary in CO_2 electro-conversion. Around 50 kW h $kg_{H_2}{}^{-1}$ is typically necessary for water electrolysis by considering the overpotential necessary. Data at the end of 2021 indicate a approximate cost of 0.21 € per kW per h (Eurostat data). Thus, around 4.5 € per $kg_{C_2H_4}$ would be necessary, even considering 100% selectivity to ethylene. The commercial value of ethylene depends on various factors but can be considered on average around 1.0–1.2 €/ per $kg_{C_2H_4}$. Thus, even considering the cost of CO_2 and the process as zero, producing ethylene by electrocatalytic reduction would become attractive only when the cost of renewable electrical energy decreases by a factor over 5, and efficiency in generating the protons necessary for the CO_2 reduction is increased. According to Fraunhofer ISE June 2021 estimations,[82] the levelized cost of electricity at the best (PV utility-scale) is between 3–6 €cents per kW per h, decreasing to 2–3 in 2040, thus in line and above with the requirements indicated above.

Note that we indicate H_2eq., *e.g.*, H^+/e^-, because the latter are those needed in the electrocatalytic reduction of CO_2. This would in part avoid the overpotential necessary to form H_2 from this hydrogen equivalent. The largest contribution to overpotential in water electrolysis, however, is related to the oxygen evolution reaction (OER). Substitution of this reaction with anodic reactions alternative to water oxidation and requiring a lower overpotential, eventually providing also a better-added value than O_2, is thus a target to decrease the overall costs. Khan *et al.*[83] indicate a 32% decrease in the energy and an 80% in the cost by anodic coproduction of glycolic acid.

In a recent assessment, Sargent's group[84] analysed the cost of producing ethylene in a neutral MEA (membrane electrode assembly), an alkaline flow cell electrolyzer, and a high-temperature SOEC (high-temperature solid-oxide electrolyzer cell). They remarked that low eEE (electrical energy efficiency), loss of CO_2 to carbonate and crossover were among the critical issues influencing the cost. In a tandem process, the first CO_2 to CO followed by CO to C_2H_4 was indicated as the solution to decrease the cost at an optimistic value of 0.8–0.9 € per $kg_{C_2H_4}$. However, this is based on the indication that it would be not possible to prevent carbonate and membrane crossover. The use of gas-diffusion electrodes and the choice of electrolyte and membrane (for example, bipolar membranes) can considerably reduce, if not eliminate, these issues. Thus, a single-cell approach, rather than a tandem one, could be still preferable.

This example illustrates the many difficulties existing in estimating the potentiality of CO_2 in the ethylene electro-conversion process. It is necessary to enter into the details of evaluations and analyse whether the assumptions and considerations made are correct or just a challenge to realize. Pappijn *et al.*[85] indicate that the electrochemical production of ethylene from CO_2 is not feasible and also has a lower CO_2 avoidance potential than the substitution of grey electricity by green electricity. However, the process scheme considered has a conventional CO_2 capture and separation step which significantly impacts the overall process ("the thermal energy required in the CO_2 capture step is equal to approximately 87% of the total energy need"). In addition, the separation section downstream to the electrocatalytic reactor is also complex, with stages of (i) gas/liquid separation, (ii) gas purification, (iii) compression, (iv) caustic wash and drying, (v) demethanization, (vi) deethanization, (vii) acetylene hydrogenation and (viii) final C2 fractioning. The challenge in all electrocatalytic devices for CO_2 conversion is to avoid a preliminary stage of CO_2 capture, *via* the use of tailored gas-diffusion electrodes which include elements for CO_2 direct capture from low-concentration streams.[86] Separation schemes, as illustrated in Fig. 1b, could be much simpler and less costly, but this depends on the operational conditions (pressurized electrolyzers) and selectivity of the electrodes. The message here is thus that there exists a potential to drastically reduce these negative elements and realize a technologically feasible process.

There are also other critical aspects such as availability and continuity of the supply of renewable electrical energy. Experience in industrial electrolyzers also indicates that water purity for the electrolyzers and the presence of solubilized O_2 in it are other factors sensitively influencing the costs, affecting stability. In CO_2 electrolyzers the TRL of development is still lower, and thus aspects related to these questions, as well as purity of the CO_2 stream, have not yet been analysed.

Note also that most of the studies are focused on the electrocatalytic reduction of CO_2 in an aqueous electrolyte, with consequent limits related to the solubility of CO_2 in water. De Luna *et al.*[81] remarked on the need to move toward flow-cell and gas diffusion-type architectures that operate at more industrially relevant current densities (>100 mA cm^{-2}). This solution will also in part reduce the purification issues in the process scheme presented by Pappijn *et al.*[85] We already, several years ago, showed that passing to this architecture is a

requirement to industrialize electrocatalytic and photoelectrocatalytic reactions.[87–89] We also showed that the products, and thus the mechanisms of reaction, are significantly modified in passing from conventional electrocatalytic studies in the presence of a bulk electrolyte to a flow-cell and gas diffusion-type architectures.

Another crucial parameter often not considered is the current density of the specific target product, because this is a measure of the productivity of the electrode and thus is a critical parameter for exploitability. Table 2 reports some selected literature results for copper-based electrocatalysts.[69] Copper is the most studied electrocatalyst for CO_2 to ethylene electroconversion. Although it is often cited in literature that copper has unique properties to form ethylene, and this concept is supported by theoretical determinations, other metals can also selectively form C2 products by direct electrocatalytic reduction of CO_2 under proper reaction conditions.[86,90,91]

Table 2 summarizes several aspects.[92–102] The first general consideration is that copper must be modified to obtain good results in CO_2 to ethylene conversion. However, a variety of modifiers have been found to significantly enhance the properties, even though these modifiers have different characteristics and mechanisms of promotion. While theoretical studies and many mechanistic hypotheses identify the selective formation in the presence of specific copper active centres,[69–80] the fact that quite different types of promoters and mechanisms of promotion equally influence the selectivity in ethylene formation puts a question mark on the mechanistic hypotheses determining the selective formation of ethylene and related electrocatalyst design indications.

The second aspect emerging from the data in Table 2 is that significantly high current densities (J) and faradaic efficiencies (FE) can already be achieved, although not always at the same time. However, quite basic conditions are required, which in general may question the stability of operations in extended continuous tests. When diluted electrolytes are used, current densities are over 1–2 orders of magnitude lower, as exemplified in the last two entries in Table 2 (selected among many others to illustrate the concept). The need for strong basic conditions, up to pH 15, is not convincingly clarified.[98] From one side, these strong basic conditions could be necessary for modifying *in situ* the electrocatalyst characteristics, such as generating a hydroxide-type surface, when the potential is applied, similarly to what we observed with *operando* EXAFS when a potential is applied to small iron nanoparticles.[103]

Negative charges generate on the electrocatalyst surface when a potential is applied to the cathode. The electron transfer to CO_2 molecules generates a negative charge. The anion-radical molecule after the first electron transfer thus tends to move far from the electrocatalyst surface, preventing further conversion if a sequential electron-transfer mechanism is present (as assumed in almost all mechanisms of CO_2 electroreduction, differently from enzymatic mechanisms[73]). This crucial aspect is typically not considered. Even chemisorption of CO_2 through the oxygen atoms[104] or in an electrolyte of carbonate ions is inhibited on a negatively charged surface. Thus, a metallic copper surface, that is typically assumed to be active in electrocatalysis for CO_2 to ethylene, would be unable to chemisorb CO_2 and reduce it, when a negative potential is applied. This crucial aspect suggests that likely an *in situ* transformation will occur[91,103] and this would be the key to the electrocatalytic behaviour, although this aspect is typically not considered even if would significantly influence the reaction mechanism.

As noted before, a very strong basic electrolyte (up to pH 15)[98] is sometimes used to inhibit the side reaction of H_2 generation and to provide the necessary ionic conductivity to sustain high current densities, but could be critical for stability and industrial exploitability. Understanding how to use reaction conditions and reactor design which are better compatible with industrial scalability while maintaining high performance is still an open question. At the same time, however, another issue to clarify is whether the use of some specific reaction conditions, such as a quite high pH of the electrolyte, could be instead related to an *in situ* dynamic modification of the electrocatalyst.[91]

The third consideration emerging from Table 2 is that experimentation with gas-diffusion type electrodes in continuous-flow electrocatalytic reactors (suitable for scale-up and industrialization), and under pressure, is still limited in the literature, although indicated sometimes by the same authors

Table 2 Selected electrochemical results in the CO_2 to ethylene conversion on copper-based electrocatalysts. Elaborated from ref. 69 with permission. Copyright @ 2021 Elsevier Science

Electrode	Electrolyte	Current density, mA cm^{-2}	Faradaic efficiency to C_2H_4%	V *vs.* RHE	Ref.
Cu nanocubes	1 M KOH	300	57	−0.75	92
Cu + Al	1 M KOH	400	80	−1.50	93
Cu modified (*N*-arylpyridinium)	1 M $KHCO_3$	320	72	−0.83	94
Cu modified (poly-*N* acrylamide)	1 M KOH	430	72	−0.97	95
Cu + iron porphyrin	1 M $KHCO_3$	300	38	−0.82	96
Optimized Cu_2O/Nafion	1 M $KHCO_3$	300	44	−0.85	97
Cu nano + PFSA ionomer	7 M KOH	1550	60	−0.91	98
Cu + Ag	1 M JOH	330	48	−0.70	99
Cu modified F	0.75 M KOH	1600	65	−0.89	100
Sn-Doped CuO nanosheets	0.1 M $KHCO_3$	16	48	−1.1	101
Nanodefective Cu nanosheets	0.1 M K_2SO_4	60	83	−1.2	102

publishing data reported in Table 2. The effect of using diluted streams of CO_2, eventually containing some of the typical possible contaminants, is also not well explored. Cross-over effects through the membrane are indicated, but often how this issue could be eliminated is not properly considered.

There are thus many aspects which still need to be developed, but the current state-of-the-art in CO_2 electro-conversion to ethylene shows that some of the targets for the process to be considered feasible from an industrial perspective have already been reached, except perhaps stability. The main limiting factor is thus the availability of low-cost renewable electrical energy, below about a few cents per kW h.

As indicated, this renewable energy cost of a few cents per kW per h is feasible, although the possibility of obtaining continuous (24 h) operations with renewable energy remains an issue. This is a requirement to reach the necessary impact on CO_2 emission reduction. In a decade from now, the share of renewable energy in the electrical energy mix will be likely not higher than one-third, and by using this share, any of the electrocatalytic processes will meet the targets of strong GHG reduction (>50–70%). The design of electrocatalytic processes integrating a PV unit, a transient energy storage unit (realizing a temporal decoupling of anodic and cathodic reactions through redox storage elements[105]), and an electrocatalytic component to perform the direct power-to-chemical storage is one of the directions to explore more systematically.

Direct electrocatalytic CO_2 to methanol. Methanol electrosynthesis from CO2 requires sixth electrons, while twelfe are those necessary to synthetize ethylene. It thus requires formally half of the electrical current to synthetize this molecole. However, the product value of methanol is around one-third of that. In addition, competitive power-to-methanol processes, developed at a pilot scale, exist. These indications strongly indicate that producing methanol by electrocatalytic conversion of CO_2 is an even less convenient direction than the already challenging CO_2 to ethylene case.

Methanol is used in current petrochemistry for different uses and is one of the chemicals with the largest prospects of growth in the near future.[106] There are two main drivers for this forecast: (i) the expected use for fuels (for direct blending or reactants to make other fuel additives) and (ii) the expanding sector of MTO (methanol to olefins) and related processes. The use of liquid fuels will be definitively depressed in the next decades, with the shift to electrical or hydrogen-powered engines. The production of olefins will be substituted by alternative low-carbon routes such as those discussed. Thus, notwithstanding the indications of an expected high compound annual growth rate (CAGR) for the methanol market, it is not reasonable to expect that its market will greatly increase in the future to justify the introduction of a new technology of direct electrocatalytic synthesis of methanol from CO_2. Rather than developing this route, it would be better to search for electrocatalytic processes directly producing the chemicals derived from methanol. Excluding fuels, in methanol to olefins the main chemicals produced by using methanol as a reactant or co-fed are, in order of relevance: (i) formaldehyde (~24 Mt per year), (ii) acetic acid (~8 Mt per year), and (iii) other chemicals such as methyl methacrylate, methyl mercaptan, methylamines, methyl chloride; altogether about (~7 Mt per year. Thus, rather than synthesize methanol from CO_2 by electrocatalysis (various reviews on this reaction have been published recently[107–111]), it would be better to synthesize directly the products of further methanol conversion, particularly formaldehyde and acetic acid.

Direct electrocatalytic CO_2 to formaldehyde and acetic acid. These routes have been explored in the literature, but comparatively fewer results have been reported concerning studies on CO_2 electro-conversion routes: (i) formic acid, (ii) methanol, and (iii) ethylene or ethanol.

The production of formaldehyde by CO_2 electrocatalytic conversion is not the subject of specific reviews and is typically also not discussed, or only marginally, in general reviews on the electrocatalytic reduction of H_2. However, as one of the main products synthesized from methane, and requiring fewer electrons with respect to methanol ($4e^-$ against $6e^-$ for the methanol case), it should be evident that more attention should be given to this reaction, even with the intrinsic difficulties, such as an easy polymerization. Formaldehyde is the intermediate in going from CO_2 to methanol in the enzymatic pathways, summarized below:[112]

$$CO_2 \xrightarrow{2e^-/2H^+} HCOOH \xrightarrow{2e^-/2H^+} CH_2O \xrightarrow{2e^-/2H^+} CH_3OH \quad (1)$$

A way to produce formaldehyde (CH_2O) from CO_2 is thus by microbial electroreduction of CO_2. However, also in this case specific studies are limited. Guo *et al.*[113] reported recently that CO_2 is converted into formaldehyde by coupled photoenzyme catalysis, although the enzyme reduction of CO_2 is predominant compared with the photoreduction. Results, however, are not optimal, with the yield of formaldehyde reaching 3.8% with the addition of 1 mM NAD^+, the oxidized form of nicotinamide adenine dinucleotide coenzyme. Liu *et al.*[114] also studied in which experimental conditions it is possible to maximize the formation of formaldehyde, rather than to arrive at the final production (methanol). However, most of the studies in this area are centred on methanol production.

Among the best results in this reaction are those of Nakata *et al.*,[115] who studied the electrocatalytic reduction of CO_2 in seawater (to increase CO_2 concentration in solution) on boron-doped diamond (BDD) electrodes under ambient conditions to produce formaldehyde. BDD electrodes have a wide potential window and high electrochemical stability, giving high faradaic efficiency (74%). The sp^3-bonded carbon of the BDD was indicated as the active centre. More recently, Pawar *et al.*[116] reported the use of a photoelectrocatalytic approach (Ca and Fe co-doped TiO_2 photoanode and Cu/rGO/PVP/Nafion multilayered hybrid composite cathode), but at the conditions of maximum formaldehyde formation (about 480 μM) the energy efficiency is low (around 20%). Thus, data for the electroreduc-

tion of CO_2 to formaldehyde are still quite limited, and the results still have to be improved.

More studies have been reported on the electrocatalytic reduction of CO_2 to acetic acid/acetate. As for the ethylene case, this synthesis requires the formation of a C–C bond. Concerning other C2 products formed in CO_2 electroreduction, it is an $8e^-$ reduction (to acetic acid) with respect to a $12e^-$ (to ethanol, or ethylene).

Acetic acid has a market value around three times higher than that of ethanol, and about 30% higher than that of ethylene, although these are average indications, depending highly on regions, time and other aspects. If we consider that the number of electrons necessary for the transformation is over 30% lower, and the higher market value, it is evident that electrochemically producing acetic acid/acetate from CO_2 is economically more interesting than the ethylene case, while producing ethanol is likely not a worthwhile area.

Ethanol could be better produced by fermentation.[117] Acetic acid could be also produced by fermentation,[118,119] and was produced by this route in the past. Although the process is well established, the main issue is the combination of separation costs and productivity. For this reason, almost all industrial production of acetic acid today is *via* catalytic routes (mainly methanol carbonylation). The fermentative route (oxidative fermentation using acetic acid bacteria) is currently mostly used only for food-grade acetic acid (vinegar). The introduction of advanced separation processes, for example by membranes, could make the fermentation route competitive. In general, the issue is the development of biofactories with an optimized integration between biocatalytic and photo/electrocatalytic routes.[29,120–122]

Acetic acid/acetate finds application as a large-volume chemical in many applications: manufacturing of coatings, greases, polyesters and sealants which are used in several industries such as electronics, automobiles, textiles, and packaging.

Nguyen *et al.*[123] have recently made an LCA comparative analysis of the production of acetic acid by electrocatalytic reduction of CO_2 (direct one-step or step-step *via* first the electrocatalytic reduction of CO_2 to CO), with respect to other products which can be obtained in the reaction (formic acid, CO, CH_4, CH_3OH, C_2H_4, C_3H_7OH). They estimated the carbon intensity (*i.e.*, global warming impact) of one and two-step electrochemical routes with respect to the thermochemical CO_2 utilization and FF-based synthesis routes. Due to carbonate formation or CO_2 crossover in one-step CO_2 electrolysis using a neutral pH membrane electrode assembly, the two-step electrosynthesis pathways (*i.e.*, CO_2 to CO in solid oxide electrolysis cell followed by CO electroreduction in an alkaline flow cell) were indicated as preferable, but as noted before the possibility of overcoming this problem (recirculating CO_2, avoiding CO_2 crossover by suitable membranes, an improvement anyway necessary) was not considered. Thus, the preferred two-step solution over the direct one does not account for possible technological advances.

Furthermore, Nguyen *et al.*'s[123] analysis further indicated that the carbon intensity of electrosynthesis products is due to a significant energy requirement for conversion (77–83% of total energy consumption for gas products) and product separation (30–85% of total energy consumption for liquid products) phases. This is again based on assumptions, such as the need to use liquid electrolytes, and the need for product recovery by distillation. As noted before, technological developments in cell design and integrated separation units could largely change the indications. Thus, the estimated cradle-to-gate carbon intensity (GWI – Global Warming Impact) should be made in the perspective scenario of technology development, which also more precisely defines the objectives. Most of the reviews and perspective papers on CO_2 do not make this effort to link needs from a techno-economic feasibility perspective with research targets. Most of these papers link to generic objectives of improving performances, rather than attempting to identify the priorities. Improving the electrocatalysts' performances such as the faradaic efficiency (FE) is useful, but if this is achieved by using reaction conditions (electrolyte, current densities, *etc.*) and materials not practicable from an industrial perspective, this could translate to a negative cost advantage. Similarly, FE itself is not an absolute value but is about electrocatalytic operations, including separation, stability, impact on raw materials and electrical energy consumption, *etc.*

A further assumption by Nguyen *et al.*[123] is that CO_2 needs to be captured from emission sources, and then this pure CO_2 stream fed to the electrocatalytic reactor. While this is the current approach, this is not a requirement. It is possible to develop electrocatalytic cells directly connected to the CO_2-emitting sources, designing more advanced devices which integrate both capture and electrocatalytic functions, operating eventually at the conditions of the emitted CO_2-containing stream. In other words, this is an aspect to overcome by proper research rather than a limit that cannot be exceeded. As should emerge from this perspective, and for this reason repeated, it is necessary to have a broad view of the problem, account for the complexity and future developments, identify the technological scenario of development, and link to them the priorities for research. Developing FF-free sustainable chemical production requires a system change and thus an approach going beyond a specific technological evaluation and a too-focused research perspective.

In these terms, another limit of Nguyen *et al.*'s[123] assessment is that not only should the cradle-to-gate carbon intensity be accounted for, but also the different "services" which can be provided by the product. Formic acid, for example, has limited uses itself and should be further converted, while acetic acid is a chemical with direct wide use.

Nguyen *et al.*[123] also compared the GWI (Global Warming Impact) of the electrochemical CO_2 conversion with that of the thermocatalytic route (from CO_2) and concerning the current (incumbent) production of the same chemical product starting from FFs. They estimated that only in the case of propanol (C_3H_7OH) are the GWI results inferior to those of the incum-

bent route, while they do not consider feasible the thermochemical conversion of CO_2 to ethanol, acetic acid and propanol. Producing propanol *via* the fermentation route results in lower GWI than the incumbent route (hydroformylation of ethylene) considered by these authors. In addition, the production of ethanol and acetic acid from the thermocatalytic conversion of CO_2 is feasible. With all these limitations, the validity of the conclusions can thus be questioned: preference of two-step *versus* direct CO_2 electrocatalytic conversion, feasibility only of production of CO and propanol, and in part ethylene by CO_2RR (CO_2 electrocatalytic reduction). We have analysed this more in detail in this assessment[123] and note the need from a tutorial perspective to enter into details of estimations, their pros/cons and methodology, *etc*. rather than using only the conclusions. All LCA, in addition, have intrinsic limits related to the database used for estimations, which become crucial in comparing technologies still at an early stage of development with well-established routes.

Dedicated reviews dealing with acetic acid/acetate from CO_2 are not present in the literature, but results on this reaction are part of the general reviews on CO_2RR. Feng *et al.*,[124] for example, reviewed results on the generation of oxygenates from the electrochemical reduction of carbon dioxide, but dedicated fewer aspects to this reaction, limited to reporting the results of Sun *et al.*[125] that reported the use of an N-based Cu(I)/C-doped boron nitride (BN-C) composite for electrocatalytic reduction of CO_2 to acetic acid. They reported a FE of acetic acid as high as 80.3% but at a low current density (about 14 mA cm^{-2}) when an ionic liquid (IL) containing LiI and water is used as the electrolyte, posing some questions about industrial feasibility. The IL was the commercial 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4).

Zheng *et al.*[126] discussed the formation of acetate/acetic acid as part of a critical appraisal of the reduction of CO_2 to C2 products focusing on the connection between the fundamentals of reaction and efficient electrocatalysts. Their approach started from an atomistic mechanism of various C2 and C3 products, to analyse the factors influencing the behaviour (local pH, overpotential, presence of surface adsorbates). However, often indications of these aspects contradict the first part of atomistic mechanisms. Also, the design principles of C2 electrocatalysts (chemical states, defective sites, nanostructure) are often not consistent with the whole set of experimental results. For example, the experimental evidence shows that the selectivity of acetate/acetic acid depends drastically on the surface coverage by CO_2 and cell design. This remark (the lack of a holistic approach considering all the experimental results) can be applied to several reviews discussing the design criteria for CO_2 electrocatalytic reduction. Another example is the review of Wu *et al.*[127] In addition, the need to approach electrocatalysis from a different perspective than just the transposition of approaches used in heterogeneous catalysis has to be highlighted.[10,22]

Some selected results are summarized in Table 3. Guo *et al.*[128] observed good FE attributed to the unique co-coordination of pyridinic N and C═O with copper whose chemical state is between +1 and +2 and the porous 3D core that is kinetically favourable for the acetate product. However, as shown in Table 3, the current density is rather low, and thus also the productivity.

Zang *et al.*[129] studied a Mo_8@Cu/TNA electrocatalyst, where TNA indicates a TiO_2 nanotube array, and Mo_8 the polyoxometalate (POM) $Cu_2Mo_8O_{26}{\cdot}2H_2O$. The current densities are not very relevant, but in addition to H_2, various other organic products were detected (ethanol, acetate, methane, ethylene, ethane). They suggested that the interface of Cu planes and polyoxometalate clusters with abundant Cu–O–Mo active sites promotes the generation of $*CH_3$ and successive coupling with CO_2 insertion, highlighting the need to realize a Cu–O–Mo interface for the rational design CO_2RR to acetate. However, Giusi *et al.*[130,131] showed that a higher FE to acetic acid (~62%) could be obtained by using Cu_2O deposited over TNA. These tests were realized in a different electrochemical set-up, without a liquid electrolyte and with gaseous CO_2 flowing through a TNT nanomembrane. de Brito *et al.*[132] instead used a photoelectrocatalytic device, reporting a FE of about 75% to acetate for Cu_2O deposited over a TNA electrode. In both these cases, thus higher FE was reported without the need to realize Cu–O–Mo active sites, and nanocomposites with a POM.

Guo *et al.*'s[128] mechanistic indications were based on theoretical – DFT (density functional theory) – calculations. The question which may be posed is whether a mechanistic interpretation is correct (need to form Cu–O–Mo sites), when higher FE could be obtained in different systems also based on copper, but without molybdenum or POM. In turn, the other question mark is whether the mechanistic approach used (by DFT) can prove the reaction mechanism.

De *et al.*[133] used a molecular manganese corrole complex for the electrocatalytic reduction of CO_2 to acetic acid. In a moderately acidic aqueous medium (pH 6), a selectivity of 63% was reported with a turnover frequency (TOF) of 8.25 h^{-1}

Table 3 Selected electrochemical results in the CO_2 to acetate/acetic acid conversion

Electrode	Electrolyte	Current density, mA cm^{-2}	Faradaic efficiency to C_2H_4%	V *vs.* RHE	Ref.
Polymeric Cu–ligand complex core–shell microsphere	0.5 M $KHCO_3$	~1	64	−0.37	128
Mo_8 clusters@ Cu nanocubes	Saturated $NaHCO_3$ solution	110	49	−1.13	129
Mn-Corrole on carbon paper	0.1 M phosphate	~0.5	63	−0.67	133
N-Doped nanodiamond	0.5 M $NaHCO_3$	~0.5–1.0	78	−0.8	135
3D 3D dendritic CuO–Cu_2O composite	0.1 M KCl	11	48	−0.4	136

(thus quite low, as indicated by the very low current density in Table 3). Genovese *et al.*[134] showed the importance of the interface with the electrolyte and of the subsequent reaction of the negatively charged radical species formed by electron transfer of one electron from the catalyst (a supported copper electrocatalyst) to CO_2.

Among the best results are those by Liu *et al.*[135] on an N-doped nanodiamond/Si rod array electrode, giving a FE of about 80% to acetate plus about 10% to formate. However, the current density is rather low (Table 3) and no further results on these electrocatalysts have been reported even by the same group. Genovese *et al.*[103] also showed a high acetic acid FE at low applied potential, deriving from the synergistic effect at the interfaces between FeOOH and nitrogen-doped carbons. Based on both calculations and experimental evidence, Fe species were indicated as responsible for producing acetic acid through a suggested multi e^-/H^+ transfer. Zhu *et al.*[136] reported dendritic copper-cuprous oxide electrocatalysts for CO_2RR, showing a low overpotential (about 0.5 V) with 48% FE to acetic acid (together with 32% FE to ethanol). While there is often the assumption that only copper catalysts can give C–C bond formation (typically assumed *via* chemisorbed CO coupling, as indicated for example by Zhu *et al.*[136]), Zhou and Yeo[137] analysed the different mechanisms of formation of C–C bonds during CO_2RR (including to form acetate/acetic acid) and the catalysts able to form C2+ products, with a focus on non-copper electrodes. They demonstrate that (i) there is no need to have copper catalysts and (ii) the reaction mechanism do not requires coupling of CO chemisorbed species. Both these indications, widely supported by theoretical DFT studies and generally assumed as valid, have proved to be not correct from an analysis of the experimental data.

In all these tests, the acetate is a product of cathodic reduction of CO_2, while Zhang *et al.*[138] attributed its formation to the crossover through the membrane of the products of CO_2 reduction (ethanol, in particular) and their oxidation at the anodic side. While crossover could be possible, this effect requires that ethanol diffuses through the membrane, is oxidized and acetate back-diffuses to the cathodic side. In addition, often no ethanol or only traces are detected. Thus, the effective role of this mechanism on selective electrocatalysts to acetate is questionable.

There are no significant relevant results in the literature regarding scaling-up and possible industrialization, as well as aspects regarding stability. The only data are from Zhu *et al.*[139] who analysed the production of acetic acid in the electrocatalytic reduction of CO rather than CO_2. They used a Cu nanocube electrocatalyst giving a FE of only about 30% in a flow cell allowing a good current density (150 mA cm^{-2}) and stability (for over 150 h), allowing production of a good concentration of acetic acid (the other liquid product is ethanol, and the other products – H_2 and C_2H_4 – are gas phase).

Note finally that we have discussed as equivalent the formation of acetate or acetic acid. Producing acetate requires a further downstream process of either acid addition (which is not convenient and sustainable from an industrial perspective) or using alternative methods for its conversion. Among them, electrochemical acidification (dialysis) is the most interesting.[140] The problem of downstream processing after the CO_2RR step has been scarcely recognized in most of the studies on the electrocatalytic conversion of CO_2 but is crucial for process economics and thus should be an integral part of the technology assessment and the reactor design. There is often the assumption that electrocatalyst selection is independent of the reactor design, which should be a later stage of development, but this is a wrong assumption.

Ramdin *et al.*[141] have specifically addressed downstream processing in the electrochemical reduction of CO_2, although to formic acid/formate rather than acetate/acetic acid. However, in terms of process engineering, the two product classes are analogous. The pH of electrocatalytic synthesis (which depends on the electrolyte solution) determines the choice of downstream operations and economics. They investigated specifically the high-pressure electrochemical synthesis because of solubility issues in realizing the high current densities required to operate at high pressure. To suppress HER, CO_2RR in aqueous media is typically performed under alkaline conditions, thus products like formic acid, which has a pKa of 3.75, will almost completely dissociate into the formate form. The selection of separation processes depends on the dissociation state of the acids. Liquid–liquid extraction is suitable for formic acid, while electrodialysis (electrochemical acidification) is preferable for formate separation. The formic acid route is more attractive than the formate one. After these separation steps, a conventional distillation allows production of formic acid with a high concentration (>85%) typically required for use or downstream further processing. While liq.–liq. extraction is more economical, realising CO_2 electrocatalysts that can operate at low pH without affecting the selectivity of the desired products is not easy, and thus it could be worth exploring solutions to reduce costs by directly integrating the electro-acidification within the electrocatalytic step.

This was analysed, among others, by Chen *et al.*[142] for the formic acid case. They have developed a robust, scalable cell architecture for the electroreduction of CO_2 by integrating bipolar membranes (BPM). An up to 90% faradaic efficiency for the conversion of CO_2RR to formate at 500 mA cm^{-2} was realized at a 25 cm^2 GDE with a carbon-supported SnO_2 electrocatalyst. A 1.27 mm-thick catholyte film was used between the bipolar membrane and the GDE. While the state of the art for CO_2-to-formate electrocatalytic conversion (FE > 90%, current densities >0.4–0.5 A cm^{-2}) already allows consideration of the industrial exploitability of this reaction, current results on CO_2-to-acetate conversion are still at much lower current densities (Table 3). The effect should thus be to address, for this reaction, the issues of productivity and cell operations in order to reach levels suitable for exploitability.

In conclusion, differently in the CO_2 to ethylene case as well as formate/formic acid production, the production of acetic acid/acetate is still at an early stage of development for industrial exploitability, even if, in general terms, it is a reac-

tion of higher potential interest with respect to others. Intensifying the R&D activities is thus necessary.

Production of FF-free aromatics raw materials. To complete the transformation to an FF-free chemical production it is also necessary to address the crucial question of producing the aromatic raw materials necessary to produce several chemicals and monomers.[2] The main aromatics are benzene, toluene and xylenes, which are almost all derived from crude oil and, in small quantities, from coal.[143] Benzene is the major raw material for the production of (i) styrene, used then to produce polystyrene, ABS (acrylonitrile–butadiene–styrene) and rubber/plastic products; (ii) cumene and phenol, used in a large variety of chemicals from healthcare products to bisphenol A, from which epoxy resins and polycarbonates are made; (iii) cyclohexane, used as an intermediate to produce nylon; (iv) alkylbenzenes, to produce detergents and surfactants. *p*-Xylene is used to make polyesters and polyethene terephthalate (PET). *o*-Xylene is used for flexible PVC (polyvinyl chloride). Toluene's major end-products are polyurethanes. This exemplifies some of the major uses of aromatics in chemical production.

The main potential low-carbon processes to produce monocyclic aromatic hydrocarbons for FF-free chemical production are the following:[143] (i) production from the lignin component of biomass,[144–147] (ii) the production of bioethanol by biomass fermentation and then conversion of ethanol to aromatics on zeolitic catalysts,[148] (iii) the production of methanol, by biomass gasification or CO_2 conversion with green H_2, followed by methanol aromatization (MTA, methanol-to-aromatics),[149,150] and (iv) the production of biomethane from anaerobic fermentation followed by methane aromatization.[151,152] There are also alternative possibilities to produce FF-free aromatics, as summarized in Fig. 6.

Still, limited studies have attempted a comparative analysis among the different possible routes to determine the preferable path on which it is possible to produce aromatic raw materials for FF-free chemical production. Maneffa *et al.*[153] have analyzed the different possibilities for the synthesis of *p*-xylene from bio-derived compounds.

The routes considered are:

1. Methanol to aromatics (MTA)

2. The production of ethanol → ethylene → 1-hexene (trimerisation of ethylene) → (2*E*,4*E*)-2,4-hexadiene (*via* disproportionation of 1-hexene) → *cis*-3,6-dimethyl cyclohexane (by cycloaddition of ethylene on the previous intermediate) → *p*-xylene (by dehydrogenation of the previous chemical)

3. Acetic acid (by carbonylation of biomethanol or by fermentation) → isobutene → isooctenes (dimerization) → xylenes (dehydrocyclization)

4. Isobutanol (by fermentation) → isobutene → iso-octene (dimerization) → *p*-xylenes (dehydrocyclization)

5. Dimethylfuran – DMF (glucose isomerization to fructose, dehydration to HMF – hydroxymethylfurfural, then hydrogenolysis) → *p*-xylene (Diels–Alder cycloaddition with ethylene then dehydration)

6. Diels–Alder cycloaddition of acrolein (from glycerol dehydration) and DMF followed by dehydration and further conversion to *p*-xylene

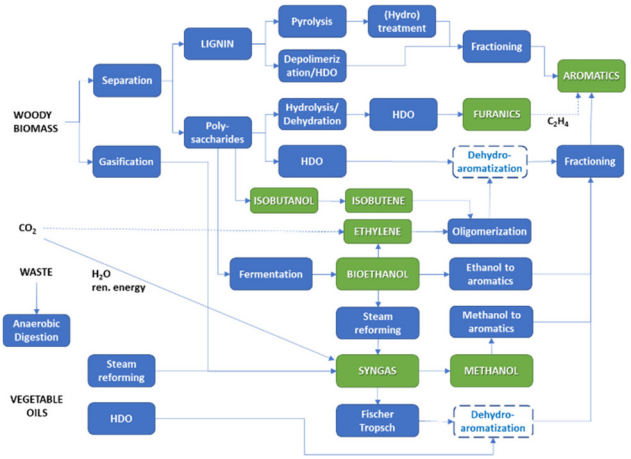

Fig. 6 Overview of different possible routes to produce FFs-free aromatics as raw materials for the chemical industry. Surrounded by a broken line indicates technologies still to be developed. HDO indicates hydrodeoxygenation.

7. Fast pyrolysis with catalytic conversion inside a zeolitic material

8. Lignin depolymerisation/hydrotreating route

All these routes thus involve complex transformations with several issues to control the product distribution and separation costs. Maneffa *et al.*[153] concluded that Diels–Alder cycloaddition of DMF with bio-ethylene and the synthesis from isobutanol are the more advanced and attractive routes in the short/medium term. However, precise data on techno-economic and environmental assessment were not given to support these indications. Even if the chemistry is known, many aspects still have to be optimized, starting from the relatively low final yields. For example, the maximum theoretical yield of *p*-xylene from isobutanol is below 40%. We believe that ethanol to aromatics (on zeolites such as modified H-ZSM-5)[154,155] is likely the preferable route, combining the use of a relatively cheap biomass source and the possibility of avoiding too many process steps. Still, too broad a range of products is formed, with a maximum aromatic yield of 23 wt% on post-synthesis modified H-ZSM-5.[156]

There are more studies on the production of the aromatic *via* FF-free methanol,[149] which can be obtained from many routes, including waste conversion and CO_2 hydrogenation. The methanol-to-aromatics (MTA) process is a promising route to produce aromatics commodities, and can also be realized in one direct step from CO_2. Among the best results directly from CO_2 are those reported by Liu *et al.*[156] using a catalyst composed of spinel structural ZnAlOx oxide and H-ZSM-5 zeolite. This catalyst shows a ~70% aromatics selectivity (on CO-free bases) with only 0.4% CH_4 selectivity in CO_2 hydrogenation (~9% conversion at 320 °C). Stability was proved for ~100 h. In syngas conversion to aromatics over Zn-doped ZrO_2 nanoparticles dispersed on zeolite H-ZSM-5,[157] with the syngas produced for example by waste gasification, aromatics with 80% selectivity at CO conversion of 20% could be achieved, without catalyst deactivation for over 1000 h.

In MTA a relatively broad range of aromatics and other hydrocarbons is obtained, while the interest is to maximize the formation of BTX (benzene–toluene–xylenes). Among the best results in this direction are those by Zhang *et al.*[158] reporting a BTX selectivity of up to ~68%, and by Wang *et al.*[159] with a BTX selectivity of ~60%. Operations at high pressure have been reported recently to give a highly selective and stable production of aromatics in MTA over ZSM-5,[160] but the best results (selectivity to aromatics up to 50%, with 20% BTXs) do not appear to be outperforming. An interesting recent result is the possibility of a computer-aided selection of the zeolite catalyst to perform "*ab initio*" zeolite design to maximize aromatics formation.[161] However, the approach has been used only to maximize DMF conversion to *p*-xylene (with best yields around 17–18%) on delaminated ITQ-2.

Benzene has been reported recently to be produced from lignin hydrogenolysis on RuW supported on a high-silica HY zeolite.[162] Yields of benzene range between 10 and 20% in the *in situ* refining of lignin, depending on the type of starting woody materials, with pine giving the highest benzene yield. Around 17 g benzene could be produced for each 100 g lignin. In general, producing aromatics from lignin has been indicated by LCA methods to offer better environmental performances than FF-based products, especially with respect to climate change.[163] Note finally that not only aromatics could be obtained by lignin conversion, but also aromatic amines.[164]

Improving the design of zeolites for all these reactions to form aromatics requires a better understanding of weakly acidic sites on zeolites,[165] because too strong acidity will lead to acceleration of the rate of carbon deposit in the zeolite pores, with fast deactivation. Quite unexplored is the possibility of using alternative microporous materials analogous to zeolites, such as the zeolite-template carbon (ZTC), which could offer also the possibility of developing electrodes combining a tailored and ordered microporosity, a high surface area and good conductivity.[166] Design of bifunctional zeolite not based on noble metals[167] also has to be improved for better control of the reaction of aromatic production. These examples highlight that many possibilities still exist for improving the design of catalysts for the selective production of aromatics not based on FF use.

In conclusion, even if the preferable route to produce FF-free aromatics has to be still identified and the performances of the catalysts need to be further improved, it appears to be a feasible possibility for the production of aromatics raw materials for FF-free chemical production. However, more attention also has to be given to developing novel innovative routes to the cost-efficient separation of the different products formed, or to develop truly selective synthesis methods.

Direct electrocatalytic synthesis of inorganic chemicals. Among the inorganic products of chemical production, two of them, namely Cl_2 and NaOH, are already produced using an electrochemical process. H_2, another main inorganic chemical, is already at an advanced stage of production using electrolysis processes and, in the future, photo(electro)catalytic ones.[63] Another major inorganic chemical is ammonia, the basis for the production of fertilizers, one of the largest volume chemicals.

The production of ammonia is one of the processes responsible for the largest GHG impact of the chemical industry, around 1.2% of the global anthropogenic CO_2 emissions. This is associated with the use of methane (or other FFs) to produce the hydrogen necessary for N_2 conversion to ammonia. A modern, optimised and highly efficient methane-fed Haber Bosch (HB) process for ammonia synthesis emits about 1.5–1.6 t_{CO2}-eq per ton of ammonia produced.[168] The Sankey diagram showing the breakdown of CO_2 emissions in a modern HB plant with respect to an electrified HB process (Fig. 7) provides relevant indications. The electrified HB process considers the production of H_2 by electrolysis, and then the use of this H_2 for the thermocatalytic synthesis of ammonia. The range of variability is associated with different sources of renewable energy used for electrolysis.

The electrified process significantly decreases the CO_2 emissions with respect to the conventional process, but still, emissions remain significantly and largely associated with H_2 generation. To decrease further the impact and reach a decrease in the GHG emissions by over 70%, as would be necessary to meet the NZE target, it is necessary to pass from the two-step electrified process (H_2 production by electrolysis, then thermocatalytic ammonia synthesis – high temperature and pressure) to the direct electrocatalytic synthesis of ammonia. In the direct process, rather than produce H_2, compress it to over 100 bars and then heat to the ammonia synthesis conditions – over 400 °C; the hydrogen-equivalent (H^+/e^-) are used in the process of N_2 conversion to NH_3. Near ambient conditions are used for electrocatalytic synthesis.

In this way, losses by overpotential (due to generation of H_2 and its activation) and operations at high temperature/pressure (and associated thermodynamic limitations on equilibriums and thus need to recycle) can be reduced. Thus, meeting the targets requires passing from two-step electrification to direct electrification. The other advantage is that direct electrification

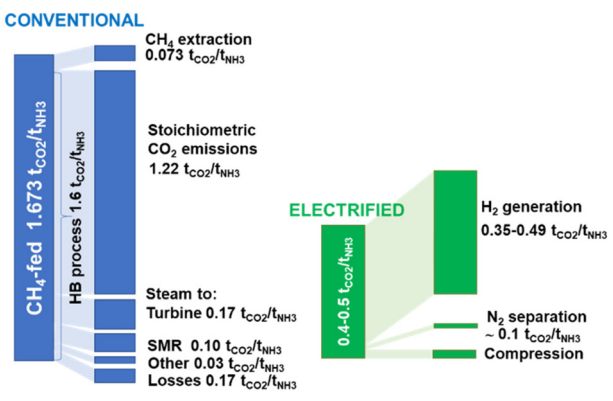

Fig. 7 Sankey diagram comparing CO_2 emissions breakdown for conventional HB process and the electrified version, where H_2 is produced by electrolysis then used in the HB thermocatalytic process. Based on the data reported in ref. 168.

is suited for distributed productions, *e.g.*, for small-scale plants, while realizing highly energy-efficient small-scale ammonia synthesis plants using H_2 produced by electrolysis is challenging. Furthermore, direct electrified synthesis of ammonia could be directly coupled to a PV (photovoltaic) module, to develop artificial-leaf type devices[63] for distributed fertilizer production[169] from air and sunlight. Note that a challenging direction, although not yet explored, is to realize on the cathodic site the N_2 reduction to NH_3[170–173] and on the anodic site the N_2 oxidation to NO_x.[174,175] By using gas-diffusion layer (GDL) electrodes and a "gas-phase" electrocatalytic reactor,[176,177] continuous operations with the recovery of NH_3 and NOx from the reactor gas streams at cathodic and anodic sections, respectively, could be achieved. By adsorbing the two gas outlet fluxes from the (photo)electrocatalytic cell in water, an ammonium nitrate fertilizer solution is produced which can be used directly as fertilizer. This is one example of the new possible directions to radically change the way we consider chemical production, by shifting to a distributed on-site model.

Many reviews have been published recently on N_2 reduction (also indicated N_2 fixation) to ammonia by a direct electrocatalytic process.[178–185] There are alternatives for direct NH_3 synthesis using renewable energy sources: photocatalytic and plasma-catalysis.[62,186–188] Note also that early studies on electrocatalytic ammonia synthesis were made by feeding H_2 together with N_2, but now this is no longer used.[189] In a sustainable framework, water appears to be the most advisable source of hydrogen atoms.

There is fast progress in the direct synthesis of ammonia, although care should be taken to avoid possible errors.[190–192] While often it appears that this is the most critical issue in ammonia direct electrocatalytic synthesis, we would stress that there are other issues. The productivities are still too low, and not enough attention has been paid to this aspect. This means that even minor contaminations could alter significantly the data. Avoiding possible errors in reporting the data is correct, but the question is different: how to make the necessary step-change to obtain more reliable results. We have remarked[171] that despite the large variety of proposed reaction mechanisms, all supported by experimental data and theoretical studies, the reported results fail within a quite restricted range of faradaic efficiency *versus* current density when the results are seen from the perspective of possible industrial exploitability. This suggests that the current studies are still unable to catch the crucial elements to reach the necessary performances for application, notwithstanding the endless reviews discussing the design of electrocatalysts for ammonia direct synthesis.

Table 4 reports a selection of literature results to illustrate further the concepts presented above. Many indications emerge from this table. The first is the very large range of materials used as electrocatalysts (just a minor subset of the large variety of materials tested) which provide relatively similar behaviour if data are analysed with respect to necessary targets (a productivity two-three order of magnitude greater, *e.g.* a current density above at least 100 mA cm^{-2}). Even if each of these results claims high performances, the results are all still far from applicability. As the very different types of materials give relatively comparable results, identification of the (highly) active sites in the selective electrocatalytic conversion of N_2 to NH_3 has been not yet successfully made, notwithstanding the claims and mechanistic indications. It may be noted that current densities are over two orders of magnitude lower than those which have been obtained in the other reactions discussed before and indicated as the target for industrial exploitability.

Most of the studies have been focused on FE, with values reported up to over 70% as indicated in Table 4. However, the results are not always reproducible. The issue, however, as emerges from the table, is that these FE results are often obtained under conditions for which the productivity in ammonia formation is quite low, often close to the detection limit. From here comes the difficulty in reproducibility. As indicated, however, this is not the crucial problem, because in any case, the results remain of limited interest. After all, what is needed is to obtain high FE, above 50% at high current densities, over 100 mA cm^{-2}. The REFUEL program of the US Department of Energy set a target of 90% FE at 300 mA cm^{-2}. Systems which can achieve, or at least indicate a possible direction to reach, these targets have been not identified. The conclusion is that it is necessary to rethink the research in this area and use perhaps different approaches.[10,171]

Note also that FE complement to 100% is due to the side formation of H_2. In an industrial device, this H_2 could be recycled in the electrocatalytic reactor. There are no studies evaluating the impact of recycling this H_2 on FE and performance. In addition, most of the studies use a liquid electrolyte,

Table 4 Selected electrochemical results in the N_2 electrocatalytic conversion to ammonia under ambient conditions (aqueous electrolytes)

Electrode	Electrolyte	Current density, mA cm^{-2}	Yield rate, nmol^{-1} s^{-1} cm^{-2}	FE to NH_3%	V *vs.* RHE	Ref.
Fe/SnO_2	0.1 M HCl	~0.5	14	20	−0.3	193
CN_x	0.1 M HCl	<0.1	0.04	62	−0.1	194
Au (faced)	0.1 M Li_2SO_4	~0.4	0.15	73	−0.3	195
Pd_3Pb	0.1 M Na_2SO_4	<0.5	0.06	22	−0.2	196
Bi nano	0.5 M K_2SO_4	~0.5	14	66	−0.6	197
Li–S doped MoS_2	0.1 M Li_2SO_4	~1.0	7.1	10	−0.2	198
B-COF	0.1 M KOH	~0.1	0.2	45	−0.2	199
FePc/pyrene	0.01 M H_2SO_4	<0.1	0.5	32	−0.1	200

from which recovery of the ammonia could be costly and may impact stability. What is necessary is to perform the synthesis under conditions (electrolyteless[201–204]) allowing continuous operations and easy recovery of the ammonia formed from the gas stream of the electrocatalytic cell.

Recent results showing the possibility of obtaining quite high selectivities using the so-called lithium-mediated ammonia synthesis (LiNR) have received much attention.[205–207] Particularly when small amounts of O_2 are co-fed and high pressure (20 bar) operations are made,[207] FE could reach a value around 80% for about 0.6% mol O_2 addition. This is presented as a breakthrough result, with a patent application titled "Oxygen enhancement of lithium-mediated electrochemical nitrogen reduction" submitted in February 2021. Current density achieved or productivity are not explicitly reported. Experiments are made in an autoclave by application of a steady current density of −4 mA cm^{-2} or a cycling method, and the experiment is stopped after 50 C of charge is passed, with part of the current used to reduce the $LiClO_4$ (Li plating). Continuous tests are thus not made, and the stability or effective performances cannot be established. By extrapolating the results given in the paper,[207] an average rate of ammonia formation (at 20 bar) of about 9 $nmol^{-1}$ s^{-1} cm^{-2} could be estimated, which is thus within the same range of best productivities reported in Table 4, but obtained at atmospheric pressure, and without applying the large overpotential (about 3–4 V) used in the Li *et al.*[207] results.

In electrochemistry, the rate of electron transfer is proportional to the overpotential. In conventional electrocatalytic tests, the overpotential should be maintained as low as possible to avoid an increase in the side reaction of H_2 formation, and thus obtain high HE. In these tests of LiNR, the trick is that the hydrogen does not derive from water electrolysis, but from a sacrificial agent ethanol, which is dehydrogenated likely to acetaldehyde. Aldehydes can easily polymerize, and thus stability could be an issue. The critical issue is the use of a sacrificial agent, the cost of which is higher than the product formed. Thus, this approach cannot be realized from a practical perspective.

An important component of the LiNR system is the solid electrolyte interface (SEI) that forms from the decomposition products of an organic electrolyte during Li deposition on the cathode. The mechanism is still a matter of question, but the first step is likely the electrochemical reduction of Li^+ ions in the electrolyte to metallic Li, which is a very reactive material. This freshly plated Li is believed to then dissociate N_2, and the N at the surface is finally reduced in a series of electron and proton transfers to form NH_3 by using a proton source like ethanol. The possibility of realizing this process under continuous conditions presents a question mark.

Cai *et al.*[206] used a different approach for LiNR. One of the sides of an electrochemical cell is in contact with a stainless steel cloth acting both as electrode and membrane through which N_2 diffuses. One side of this membrane is in contact with N_2, the other with the electrolyte and Li deposit on it. The performances reported are of slightly better productivity (~25 $nmol^{-1}$ s^{-1} cm^{-2}), but lower FE (~40%). The overpotential is quite high, at a fixed potential of −6.7 $V_{Ag/Ag+}$ used in these tests. Ethanol is also used as a sacrificial agent (proton donor).

A closer analysis of these results on LiNR thus indicates that they are not a true breakthrough and the issue of developing novel approaches for ammonia direct synthesis remains. It is thus probably necessary to reconsider the whole approach and explore new directions, as well as to analyse from a more critical perspective the whole set of results and possibilities of the approach. Few studies have attempted this effort. Among them is the review by Martín *et al.*[208] which used performance maps to analyse the gap concerning practical implementation and identify sources of inefficiency. Among the novel directions that could be mentioned in the ammonia synthesis is the use of an H_2-permeable nickel membrane/electrode that spatially separates the electrolyte and hydrogen reduction side from the dinitrogen activation and hydrogenation sites.[209]

The impact of FF-free chemical production

To analyse the potential impact of FF-free chemical production, the mapping of the global flow of chemicals prepared by Levi and Cullen may be considered.[210] Although the data refer to about one decade ago (the year 2013), this analysis could be still considered valid and no further attempts were later made to update the data. Fig. 8 reports the summary of

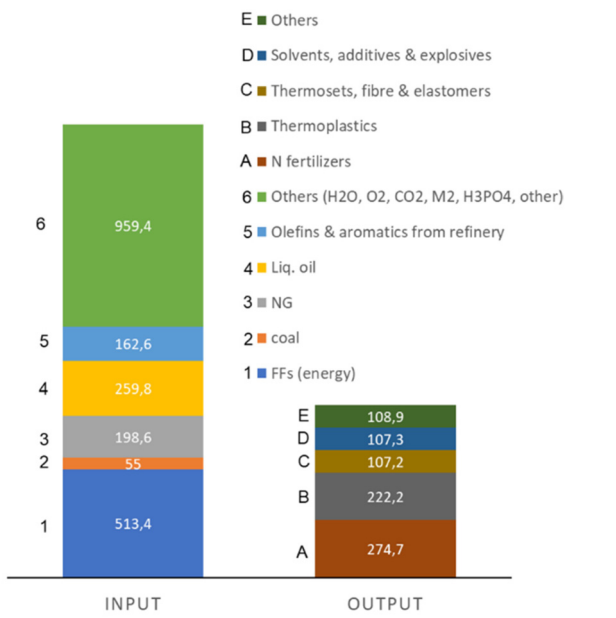

Fig. 8 Summary of input and output data (M ton per year) reported by Levi and Cullen[210] in mapping fluxes in chemical production. Output data do not consider secondary products such as CO_2, H_2O, HCl, $CaCl_2$, *etc*.

the input and output data for chemical production reported by Levi and Cullen.[210]

What is evident from Fig. 8 is that when secondary products are not considered, only about one-third of the FFs are incorporated in the final products of petrochemistry. However, part of the use of FFs as an energy source cannot be substituted by RES only. The target of 70% cut of CO_2 eq. emissions in the chemical industry thus also requires reduction of the use of FFs as carbon sources, by closing the carbon cycle and using bio-based raw materials. By considering an average factor of 1.3 CO_2 eq. ton emitted per ton of fuel combusted, around 470 Mt per year CO_2 eq. could be saved. We can also consider a possible saving in the production of N fertilizers of ~50% using electrified production, saving around 130 Mt per year CO_2 eq. By introducing direct electrified processes using alternative carbon sources it may be estimated that an additional 200–230 Mt per year CO_2 eq. emissions could be saved. Thus in total, the potential cut is around 830 Mt per year CO_2 eq. emissions, which corresponds to a reduction by about 70% of the total emissions by chemical production. It is also evident that it is not possible to meet this target by electrification of process units alone.

Sustainability of the transition to a fossil-free chemical production

After having examined (i) the socio-techno-economic motivations, (ii) the feasibility of this objective and (iii) the potential impact as well, it is necessary to discuss briefly whether the transition to a fossil-free chemical production is sustainable. A sustainable transition happens when economic, environmental, and social improvements are realized at the same time. The question of whether the transition to a fossil-free chemical production is sustainable must be thus addressed in a joint manner from these three perspectives. In addition, a deep transition requires the synchronization of the development of many technologies together with the economic and social elements.[211] Thus, the technological and scientific advances must be put in this general perspective (i) to identify whether the directions investigated are sustainable, (ii) what are the gaps, limits and opportunities, and (iii) whether the timing for their implementation is compatible with the necessary synchronization with the other elements of the deep transition. The main motivation for this perspective is to provide the elements for this holistic analysis; the scientific and technological advances alone cannot provide indications of whether this deep transformation in the chemical production, in parallel with that in energy, is sustainable and what the conditions are to improve the sustainability. Thus, scientists must be aware of the general context to contribute effectively to the implementation of the transition. Note that a perspective on future, long-term transformation necessarily contains personal elements of evaluation, which depend on the scenario assumed and related uncertainty and assumptions. For this reason, even if in part the elements discussed here are personal, they are mediated by the larger on-going discussion in the frame of the large initiative SUNERGY (fossil-free fuels and chemicals for a climate-neutral Europe; **https://www.sunergy-initiative.eu**). As part of the related coordination and support actions (CSA) SUNER-C, a strategic roadmap for the transition toward a fossil-free EU economy, is in preparation.

A first general question concerns what is a fossil-free sustainable chemical production. The discussion in this perspective assumes that to meet the NZE targets by the year 2050, it is necessary to achieve by this year a substitution of over 50% in FF use in the chemical industry (at least in Europe). This value is above the 30% target already indicated a decade ago by industrial organizations such as CEFIC (European Chemical Industry Council) as part of large initiatives such as SusChem, later becoming A-SPIRE. Although tight, the 50% substitution, in view of the acceleration in recent years on energy transition, seems an acceptable target also from an industrial perspective. Completely fossil-free chemical production could be realized thus only beyond 2050. It must also be recognized that the transition to fossil-free chemical production will be realized when investment in new plants will be only on technologies not based on FFs as raw or energy materials. However, plants using old technologies based on FFs will still be operative. A typical amortization time of chemical plants is over 20 years.

To produce any chemical, one needs raw materials, energy and reactors that realize the defossilization of the chemical production. Thus, a fossil-free chemical production process needs to defossilize all these elements to be sustainable. It may be estimated that by the year 2050, the green electricity share in the energy mix will be in the 70–90% range, depending on the scenario assumed.[213] However, without the introduction of effective energy vectors (solar fuels), the coupling of chemical production (and in general of energy-intensive industries[9]) and RES will be not effective. Thus, the sustainability of the transition to fossil-free chemical production will depend on the acceleration of the technologies to produce solar fuels (also called e-fuels) on a large scale. A crucial element to realising this objective is to decrease the costs of production while at the same time increasing the energy efficiency of the process. As mentioned in the previous section, avoiding the production of molecular H_2 and instead using the hydrogen-equivalent H^+/e^- is an important factor to increase energy efficiency. By coupling with the process intensification, developing directly the second-generation electrocatalytic routes rather than implementing the first-generation technologies (so-called power-to-X) is one of the critical elements to accelerating the process.[22] However, discordant opinions still exist on this question.

In addition, a process using only electricity, but not also defossilizing all the other process and material components, realizes only in part the sustainability objective. Electricity should be generated in a sustainable way, as should the raw materials for the process. Chemical production is a chain process, and for this reason we addressed here especially the building blocks for chemical production, *e.g.*, olefins, aro-

matics, and syngas, evidencing that not only energy but also the input raw materials should be fossil-free or based on carbon circularity.

At the same time, new process performance indicators such as (i) efficiency in energy and carbon circularity, (ii) overall degree of substitution of FFs, and (iii) sustainable energy transition readiness[212] should be introduced to better monitor the transition.

Therefore, is "fossil-free" sustainable? To reply to this final question, it must be noted that this transformation of chemical production is likely to be irreversible, and driven only in part by the need to reduce GHG emissions. The main economic drivers are geopolitical (security) and the change of the windows of opportunity for using FFs. From a social perspective, there is a need to change the modality of production and for better integration with local resources and reduction of the environmental impact of large plants. The sustainability of this transition thus derives from other aspects, rather than only from specific technological aspects. The assessment thus requires the use of new methodological approaches beyond the conventional.[214,215] However, a main limiting factor appears to be the rate of technological development for the required new processes. Accelerating this development requires a better identification of the key target objectives beyond the scientific and technological ones.

Conclusions

Chemical production needs to significantly restructure the modalities of production to meet the NZE targets, and in particular, accelerate in moving to FF-free production. This perspective attempted to analyse the status, gaps and perspectives of progress in this direction, noting also that it is an opportunity to develop a novel model of chemical production and create innovation and benefits for society. Defossilization of chemical production is a challenge and requires the combination of electrification of the chemical processes with the direct electrification of the catalytic reactions. Although challenging, accelerating the progress in the direct electrified processes is also a necessary condition to meet the target of NZE in 2050, as shown from the analysis of the potential impact of these technologies in reducing CO_2 eq. emissions from chemical production.

Electrification of the process units, and in particular of the chemical reactors, requires overcoming the simpler approach of just providing the heat of reaction by electrical heating rather than by burning fossil fuels (electrical *versus* fired furnaces). More advanced approaches require redesigning the catalyst and the reactor itself to take full advantage of the possibilities of overcoming heat transfer limitations and realize tailored thermal gradients between the catalyst surface and the fluid phase.

Direct electrification of the processes entails developing novel modalities to supply directly the energy for the chemical transformations. We have focused the discussion on electrocatalytic solutions because we commented that this is the technology that likely will be first introduced commercially in a broad mode, while other technologies such as photo- and plasma-catalysis will require a longer time for application or wider use out of specific cases. To focus the discussion, only the most relevant cases for defossilizing the chemical production were analysed: (i) light olefin production, (ii) direct synthesis of main intermediates such as formaldehyde and acetic acid, and (iii) the production of aromatics (BTX) alternative to those starting from FFs. Some considerations on the electrocatalytic production of methanol from CO_2 were also given, although we believe that there are better alternatives for this reaction. The analysis of the status of research aimed not to provide a status of the art, but to identify the key elements to assess whether in the short–medium term introducing these technologies will be feasible. Also, indications of areas to foster research activities were given.

The analysis of the direct electrocatalytic synthesis of inorganic chemicals, in particular ammonia to produce fertilizers, instead reveals that current results are still quite far from the possibility of applications, noting that, however, changing the direction of current approaches and exploring new solutions will be likely necessary.

In conclusion, the analyses presented in this perspective show that proceeding towards defossilization of the chemical production may result in an over 70% cut of the current greenhouse gas impact, with a saving of over 800 Mt per year CO_2 eq. emissions. Not only is an intensification of the research necessary, but also a holistic system approach. As noted in this paper, often this vision is missing or partial, and the scientific development is focused on specific aspects which may not be the key factors determining the possibility of accelerating the development. This paper aimed to provide at least some elements allowing researchers to have a more comprehensive view of gaps, limits and possibilities in moving to FF-free chemical production, and explained also why this conversion is necessary and the opportunities for innovation and transformation of the modalities of products it offers.

Abbreviations

Acronyms

BDD	Boron-doped diamond
BN-C	Boron nitride
BZVYYb	$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (doped barium zirconate)
CAGR	Compound annual growth rate
CO_2RR	CO_2 reduction reaction
COTC	Crude oil-to-chemicals
CSA	Coordination and support actions
DFT	Density functional theory
DMF	Dimethylfuran
eEE	Electrical energy efficiency
EXAFS	Extended X-ray absorption fine structure
EU	European Union
FE	Faradaic efficiency
FFs	Fossil fuels
GDL	Gas-diffusion layer

GHG	Greenhouse gas
GWI	Global warming impact
HDO	Hydrodeoxygenation
HER	Hydrogen evolution reaction
HMF	Hydroxymethylfurfural
LCA	Life-cycle assessment
MEA	Membrane electrode assembly
MSW	Municipal solid wastes
Mt	Million tons
MTA	Methanol-to-aromatics
MTO	Methanol-to-olefin
MW	Microwave
NZE	Net-zero emissions
OER	Oxygen evolution reaction
PBSCF	$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (porous double perovskite)
POM	Polyoxometalate
PSA	Pressure swing absorption
PtX	Power-to-X
PVP	polyvinylpyrrolidone
R&D	Research and development
rGO	Reduced graphene oxide
RE	Renewable energy
RES	Renewable energy sources
RF	Radio frequency
SMR	Steam-methane-reforming
SOEC	Solid oxide electrolyzer cell
TNA	TiO_2 nanotube array
TOF	Turnover frequency
TRL	Technology readiness level
ZTC	Zeolite-template carbon

Author contributions

All authors equally contributed to preparing and revising this manuscript.

Conflicts of interest

There are no conflicts to declare.

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