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Chemical engineering role in the use of renewable energy and alternative carbon sources in chemical production

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Abstract

There is a demand for new chemical reaction technologies and associated engineering aspects due to on-going transition in energy and chemistry associated to moving out progressively from the use of fossil fuels. Focus is given in this review on two main aspects: i) the development of alternative carbon sources and ii) the integration of renewable energy in the chemical production. It is shown how addressing properly these aspects requires to develop also a) new tools for chemical engineering assessment and b) innovative methodologies for the development of the materials, reactors and processes. This review evidences the need to accelerate studies on these directions, being a crucial element to catalyze the transition to a more sustainable use of energy and chemistry. It is remarked, however, the need to go beyond the traditional approaches, with some examples given. In fact, the presence of radical changes in the way of production is underlined, requiring thus novel fundamentals and applied engineering approaches.

Keywords: Chemical reaction engineering, Sustainable chemistry and energy, Waste-to-chemicals, Electrocatalysis, CO_2 and biomass valorization, NH_3 direct synthesis

Background

There are increasing evidences of an irreversible and fast-proceeding transition in energy and chemical technologies [1–3], characterized from the progressive substitution of fossil fuels and the introduction of renewable energy sources (RES) and alternative carbon feeds [4–8]. While still several scientists argue if and when this transition may occur, new investments are already in this direction. In addition, looking at the past decade, most of the negative opinions in terms of growing rate, due to supposed too high costs, were disavowed from recent data [4]. There are clear complex economic aspects determining the transition to novel energy and chemical production systems, but also technological facets. In fact, this transition does not imply the use of only the current available technologies in the area of chemical engineering, with just some adaptation, but involves a cultural revolution in terms of way of production [5, 8].

It is thus necessary to understand where are the bottlenecks, both in terms of fundamental knowledge and technological aspects, limiting the possibility to realize the challenges related to this transition and reach the target to make sustainable and economic these novel technologies. Even if there are increasing papers and reviews in this area, for example on photocatalysts for solar-driven overall water splitting [9] or photoelectrochemical water splitting [10], they are still oriented to analyze only the scientific aspects, including for example the type of materials to use [11, 12], rather than to present an holistic view of science and technology aspects. These two aspects should be developed in an integrated manner, rather than sequential, as exemplified from the development of photoelectrocatalytic materials and devices [13].

In addition, still often the specific research directions are not based on an analysis of how the technology should be implemented. For example, producing H_2 and O_2 from water splitting, without generating them in physically separated zones, creates major issues of safety due to the formation of H_2-O_2 explosive mixtures and

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relevant costs for downstream separation to reach the required purity. In addition, producing H_2 which has to be used later to hydrogenated CO_2, rather than converting directly CO_2 in photo/electrocatalytic devices, has major costs related to the energy necessary in producing, compressing and catalytically use H_2 to convert CO_2. There are also often relevant aspects underestimated. For example, under practical use, temperature of operation of photoelectrocatalytic devices, under full solar irradiation, may easy reach temperatures above 60–80 °C, while several of the materials proposed for these cells are not stable above 50 °C [13]. Materials development should be related to engineering and operations of the device. There are several of such a type of examples, in which research, even if excellent from the scientific perspective, is not put in the right technological perspective.

While progresses in fundaments are always necessary, there is the need to accelerate the development of the technologies enabling to meet the necessary targets, in the case of energy and chemistry in transition. Note also that a successful transitional strategy requires identifying critical processes in a timeline perspective, with solutions for short-, medium- and long-term [14]. The crucial point is that cost-effective solutions are only those integrating within the current systems and value chains, to minimize investments and thus reduce the initial cost barriers. A proper synchronism between technological capabilities and socio-economic context is the decisive issue.

We feel that today the limiting factor is the capability to identify properly the key aspects on which focus development areas from the timeline perspective of a fast evolving scenario for chemistry and energy in transition. This review will thus analyze, from a personal perspective, the possible impact on chemical reaction technologies deriving from the transition in energy and chemistry, with focus on needs, gaps and opportunities.

Developing alternative carbon sources

Current petrochemistry is largely based, over 95%, on the use of fossil fuels, particularly oil [15–17]. There are various motivations indicating the need to decrease this very high dependence. Among them: i) decrease greenhouse gas emissions in order to contribute to climate change mitigation and to reach CO_2 emission targets, ii) security and diversification of resources, iii) promote rural development by using the local resources, and iv) use of C-sources less depending on fluctuations and uncertainty in future costs of fossil raw materials.

It is often argued that cheap oil will be still available in the future to make useless the development of alternative routes. The same argument was used up to few years ago to indicate that energy from fossil fuels would remain also in the future the most competitive one.

Recent reports like that by IRENA [4] have demonstrated that instead already today this is no long valid. In the area of petrochemistry, uncertain in predicting future costs is already a major factor determining investments in new plants, with a panorama where very few new technologies have been put on the market in the last decade.

The future decade for chemical companies is market from the need to reinvent their interface with oil refining and manage the transition to a circular economy [18]. In fact, the last decade has been characterized for petrochemical companies from an erosion in the product margin, due to low-cost of feeds. Consequently, new models for value creation are necessary [18], because the advantaged-feedstock-opportunity window is closing.

Crude-to-chemicals (COTC), i.e. direct production of chemicals and petrochemicals such as olefins and aromatics directly from crude oil, as opposed to via thermal cracking of naphtha/ethane (for olefins) and via traditional refining reforming (for aromatics), is one current industrial tendency [19], together with the development of direct routes for methane to olefins and aromatics [20, 21]. Silura OCM (oxidative coupling of methane) process is one example of technology under development attracting increasing interest. On the other hand, these technologies are interesting for countries with low fossil fuel costs and one major challenge is the expected high capital investment required to construct the plants. In fact, an opposite tendency for chemical industry is to reduce the rising CAPEX costs [18], even more critical when cost forecast are difficult, and thus to adopt strategic agility [22], i.e. the capability to rapidly transform product and service portfolios in response to dynamically changing market and stakeholder needs.

Olefins and aromatics could be produced alternatively from CO_2 and H_2, also in direct processes [23], and these technologies are instead suitable for distributed, small size, productions. Worth to note, the range of possible investors for the latter type of technology is much larger than the quite limited type of investors for COTC and OCM technologies, which, in addition, will have internal competition (they own also current technologies to produce olefins/aromatics). There are additional benefits in terms of incentives for CO_2 reduction: i) promotion of bioeconomy (CO_2 could derive from biogas or fermentation processes) and integration with renewable energy sources [24, 25], ii) integration within local economy, iii) promotion of circular economy, etc. Thus, it may be argued whether COTC and OCM technologies will be game changer for chemicals industry, as announced, or instead, more likely, just a piece in the puzzle for transition in economy.

The main difference between the two approaches, apart from large vs. small-medium sizes plants, is that COTC

and OCM aim to reduce costs by using less-expensive raw materials (crude oil rather than naphtha, methane), although still based on fossil fuels, with thus a cost highly fluctuating and unpredictable in trend. CO_2/H_2 process is instead using a waste raw material (CO_2), with very low cost (some even negative considering carbon taxes) and another product (H_2) which could be manufactured using renewable energy sources, which are currently already competitive (in some cases) to the use of fossil fuels [4]. In addition, COTC and OCM needs to be produced in large plants, with costs of transport of chemicals, safety and geopolitical issues. Distributed processes allow instead a much better integration into local economies, including aspects related to circular economy [26]. It is evident that there are two different approaches, with the latter (producing raw materials for chemicals from waste and renewable energy) being based on a different, more sustainable economic model of development.

The analysis of the two production models should be thus not based on the traditional economic models and concepts, such as scale-economy. It is necessary to use new assessment tools, which include the capability to analyze socio-economical macro-trends, market evolution, competitiveness related to entire ecosystems, sustainability and integration into territory (rather than globalization), non-linear dynamic of changes and costs evolution, extended life-cycle cost and social analysis [18, 27, 28].

Therefore, new techno-economic engineering assessment tools should be developed. In transition periods, new conceptual assessment modes, including to evaluate the feasibility from a chemical engineering viewpoint, are necessary and it is historically demonstrated that in the absence of this approach a company may rapidly lose their market positions being their innovation capacity (a crucial aspect in chemical production) rapidly lost [17].

Waste-to-chemicals
Waste-to-Chemicals (WtC), as argued from above analysis, is an important element of the strategy to diversify carbon sources for chemical production. Biomass use is another relevant component of this strategy [25, 29–35]. However, when based on dedicated biomass (i.e. grown for the specific use), the negative implications on land change use and competition with other utilization, the impact on water resources, the relevant greenhouse gas emissions and high costs related to biomass growing, harvesting and pretreatment (for example, drying, size reduction, operations to improve processability) have to be taken into account.

From a process engineering perspective, the major issues are related to the presence of a complex matrix, which should be transformed to high purity chemicals in the presence of several contaminants, which can influence the use of catalysts. Solutions have been identified and made possible, but in general terms, this translates to high costs of production. Therefore, differently from a decade or more ago, when a large optimism was present, today the general perception is that the production of chemicals directly from dedicated biomass sources is applicable in some selected cases, but is not a general solution.

To be competitive to fossil fuels use for chemical production, it is necessary to i) use quite cheap raw materials, ii) integrate well into a regional strategy (also in terms of plant size), including circular economy, iii) use technologies flexible in handling a variety of biomass sources, and iv) be flexible in the production of different chemicals, minimizing costs for operations, especially purification and separation [36]. The use of waste biomass, which includes, but is not limited to, the organic fraction of municipal solid waste – MSW, which is called in different ways, one of them being RdF (refuse-derived fuel), is clearly an opportunity as a low cost raw material. In fact, it is a side production with a cost for disposal. Its valorization is often limited to thermal incineration. There are various attempts for alternative valorization methodologies to create a waste biorefinery [37, 38], but reuse is limited to very specific type of biomass waste. For general purpose technologies, following above indications, it is necessary a process technology able to handle a variety of waste sources, including MSW, to reach the necessary dimension for a regional waste biorefinery, but minimizing the transport of raw materials from long distances, i.e. less than about 100–150 km.

There are essentially two routes to produce chemicals from organic waste, particularly from MSW and excluding reuse or recycling technologies which are tailored for specific waste and not suited for mixed wastes: pyrolysis [39–41] and gasification [42–44]. By (fast) pyrolysis a liquid fuel and a gas component, with the former especially characterized by a large range of products and quite low quality, are produced (with eventually also a solid residue). Severe upgrading treatments are necessary, and the pyrolysis liquid product can be essentially used only as fuel. The syngas instead produced in the gasification process can be easier purified and further processed to produce, in a flexible way, different chemicals or fuel components [36], by using essentially available technologies. This flexibility is an important added-value term allowing a much better tailoring to different demands. This is a crucial aspect to minimize developing costs for WtC, by adapting to the large variety of locals demands. We thus limit the further discussion to waste gasification as the first step, to produce syngas to be further converted to different chemicals.

Options in gasifiers for the WtC process. Gasification can be considered a process in between the endothermic anaerobic pyrolysis process (typically occurring in the 400–700 °C temperature range), and the exothermic combustion process with excess of air (800–1400 °C temperature range). The latter produces a hot gas to be used only for electrical energy generation or heat recovery. In gasification, instead, a syngas (a CO-CO_2-H_2 mixture), with CO_x to H_2 ratios depending on operation conditions and feed, is produced by using a controlled air or O_2 feed. The oxygen is typically one-fifth to one-third of the stoichiometric amount. Steam and CO_2, in some cases, are also co-fed. The heat for gasification derives from the partial biomass combustion in the gasifier.

Biomass gasification has been extensively analyzed and discussed [44–46], but the used of mixed feeds, particularly containing the organic fraction of MSW, determines specific issues [47–49]. There are various crucial aspects in the design of the reactor: i) the gasifier should be designed to produce a tar-free syngas, because otherwise downstream cleaning is costly, ii) the formation of CO_2 should be minimized, iii) the inorganic part of the biowaste should be eliminated in a form allowing an easy disposal, and iv) pretreatment of the biowaste should be minimized as much as possible.

Different gasifier designs are used for biomass, the most common being, in the order, a downdraft fixed bed, fluidized-bed system (bubbling/circulating or dual) and an updraft fixed bed [45]. Fluidized beds for gasification processes allow high conversion and low tar yields, due to high heat and mass transfer rates, excellent gas-solid contact and good control of temperature. Besides the higher reactor costs and operations, biowaste should be grinded and sieved to small particles of uniform size, requiring additional costs.

Plasma gasification is of rising interest, for the possibility to obtain complete cracking of tar compounds and high gas yields [50]. Microwave plasma shows various advantages with respect to alternative ways to produce the plasma [51], but still there are many challenges to solve for industrial implementation. Gasification in supercritical or near-to-supercritical water [52–55] is another valuable option, but also having main challenges related to cost, thermal efficiency, plugging and corrosion problems.

The general question is that may be often unclear when and for which cases these different options should be applied. There are clear scale-up and cost issues, and different situations for which one technology should be preferable over the other [56]. Most of the considerations, however, refer to either gasification for energy purposes, or for H_2 production, with the production of optimal syngas production and integration

with downstream processing to valuable chemicals scarcely considered. There are specific, but interesting cases to consider, as the MSW treatment in small touristic islands, where the produced MSW actually needs to be costly transported by ship to remote areas for disposal. The gasification in supercritical water allows to have compact reactors, and reduce downstream cleaning processes. The syngas could be upgraded to methane for local use, being these islands not reached by the natural gas grid. This is an example of a case when a technology otherwise too costly can be instead considered.
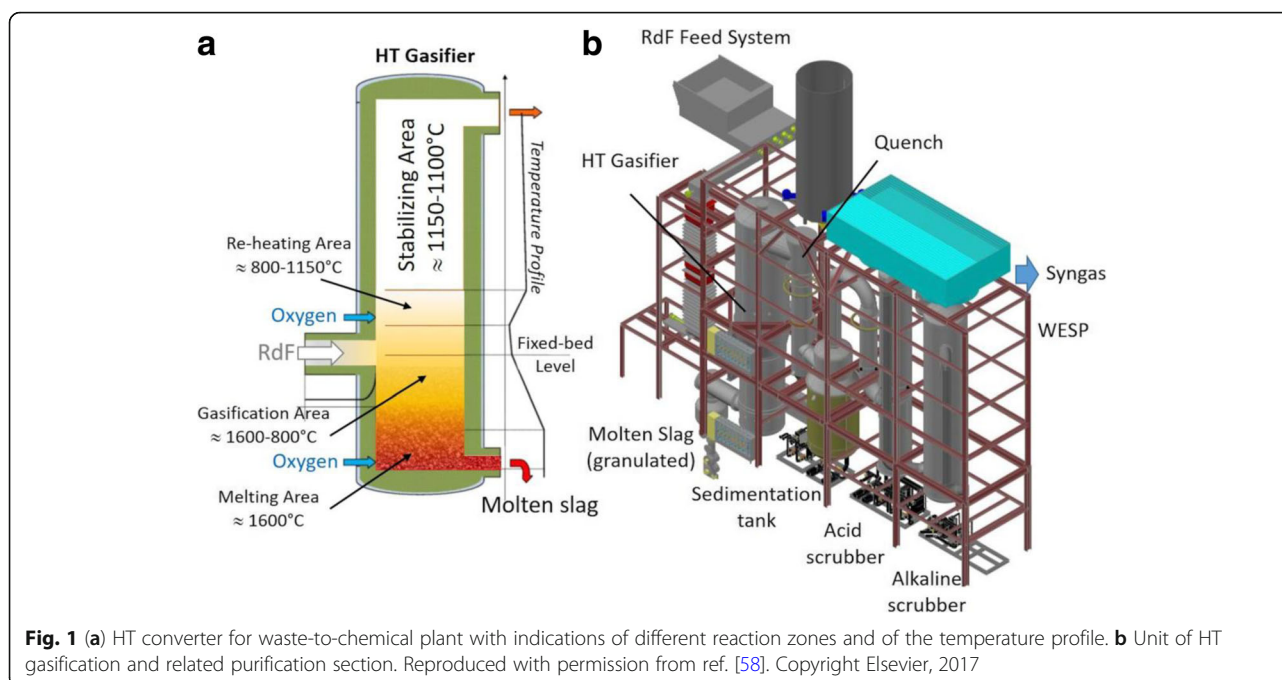
The missing knowledge are thus in suitable multicriteria assessment tools able to guide selection along the different solutions and technologies, and to identify the engineering aspects limiting the overall performances. Robustness, minimization of downstream operations, flexibility in variable composition feed handling, minimization of sludges downstream treatment, safety aspects are some of the keyword to consider for the selection.

We believe that based on these aspects, the use of a high temperature (HT) converter as that presented in Fig. 1 is preferable [57, 58]. A temperature gradient is present along the vertical axis with two oxygen injections in the heating (800–1000 °C) and melting (1000–1600 °C) areas. The biowaste (RdF) is fed from the side. The partial oxidation leads to the formation of a syngas, moving to the upper part of the reactor (stabilization area), where the temperature is above 1000 °C to crack the tars and eliminate possible toxic molecules such as dioxins and furans. The sludges are removed from the bottom (melting area) where temperatures of about 1600 °C are maintained, to allow discharge of molten slag, which by rapid cooling could be easy vitrified and made inert, for safe disposal. A relevant advantage is that the reactor allows to feed relative large particles, and thus avoiding grinding costs.

By using RdF, a typical composition of the syngas produced is the following (% vol): CO_2 8–16, CO 37–43, H_2 36–40, H_2O 6–8, with few percentages of N_2, O_2 and methane. The use of RdF and other biowaste is possible, with influence on the composition of the syngas. Temporal variations in the syngas flowrate and composition derive from the non-uniformity of the reactor bed, related to the use of large and non-uniform in size RdF particles. The partial clogging of the bed (bridge formation) later collapsing, is also another mechanism causing variations of syngas. However, a dimensioned downstream gasometer and operations with multiple parallel units, can avoid that this could be a problem in operations.

There are some main issues in this reactor. The first is that the very high-temperature operations create problems

Fig. 1 (**a**) HT converter for waste-to-chemical plant with indications of different reaction zones and of the temperature profile. **b** Unit of HT gasification and related purification section. Reproduced with permission from ref. [58]. Copyright Elsevier, 2017

of lifetime of the refractory materials used for the reactor walls, with thus the need of frequent maintenance. The second, is that modelling of this type of gasifier is difficult and thus of its optimization. The third issue is related to the possibility of using catalysts to increase conversion and reduce the temperature of operations.

Catalytic gasification is a valuable option to promote energy efficiency [45, 59, 60], but only in few cases it is applied to improve MSW gasification. Ni-based catalysts [61, 62] could be used, but they cannot be utilized in a gasifier as that shown in Fig. 1. Low costs catalysts should be used to be continuously co-fed with RdF, remaining then in the molten slug. Olivine or similar natural materials, which are available in large amount at low cost, could be used [63, 64]. Alternatively, a catalytic bed at the top of the gasifier could be used to improve the polishing of the syngas, but catalysts stable at high temperature and to the presence of fly ashes, tars, metals and salts should be developed.

Among other aspects, these three areas evidence who new chemical reaction technologies challenges are opened from the development of new technologies for using biowaste as carbon source.

Downstream processing for WtC

The syngas from the HT converted contains various impurities, which typical values (mg/Nm^3) are the following: sulphur compounds (H_2S 100–1500, COS 10–150, < 10 for other S compounds), small acids (HCN < 10, HCl < 5, HF < 1), metals (Hg < 0.2, Ti + Cd < 0.2, heavy metals < 1) and particulate matter (< 3). These impurities

should be removed before the downstream catalytic processes (Fig. 1b), with the severity of the purification depending on the sensitivity of the catalysts to the poisoning by these contaminants.

Downstream operations to upgrade syngas to chemicals are in principle similar to those already available, but with catalysts and operations that should be specifically tailored for four aspects: i) the typical higher CO_2 content with respect to current operations, ii) the higher presence of impurities, iii) the need of optimal operations in smaller reactor units and iv) fluctuations in the feed (flow rate and composition). These fluctuations can be minimized by a downstream gasometer, but remain higher than in conventional reactors, for example for methanol synthesis. Also in this case, thus new dedicated engineering solutions have to be developed.

The syngas after purification and adjustment of the CO_x/H_2 ratio, is sent to a conversion unit to obtain different possible chemicals, ranging from fuels to raw materials for chemistry and fertilizers. Methanol, urea, H_2, CH_4, olefins, aromatics are some of the possibilities, starting from RdF. They are feasible from a techno-economic perspective [36, 57, 58]. The use of mixed RdF and biowaste from agro-food production is also possible. In addition, with respect to incineration of the same waste, there are environmental advantages. For example, in waste-to-urea process, a reduction of about 0.8 tons of CO_2 emitted per ton of urea produced can be estimated [57].

This short excursus on some aspects of the development of novel routes for the use of alternative carbon sources evidences thus that many scientific and technological

questions are opened by addressing this possibility. The aspects discussed are examples, and will thus not exclude other areas. However, already they remark the complexity of the problem to be addressed in a short term. It is thus very important to focus the analysis on the most critical aspects, and guide scientific advances by using a more holistic view of the full problems.

Integration of renewable energy in the chemical production (electrify chemistry)

The direct use of renewable energy sources (RES) in chemical production, i.e. electrification of the chemical industry, is another great challenge crucial for chemical engineering. Rather than use heat (produced from fossil fuels) to run operations, electrical energy (deriving from renewable sources) should be used. This is not only a technological change in supplying the energy for the chemical transformation, but determines a full change in the engineering of chemical processes design, where heat recovery and transfer is a major designing element and one of the key factors determining the need to have large plants.

Moving in this direction will allow passing to plants optimal for small-medium size (distributed) productions. Even more important, the scale-up in electrocatalytic processes is by parallel units, differently from the conventional approach. Parallelized production will permit a much greater flexibility in production (to follow better market demands and fluctuations) and especially a faster time to market. CAPEX is higher, but compensated from above advantages. Thus, electrification of the chemical industry is not only a technological change, but a full transformation in the engineering, design and marketing of chemical processes. As commented earlier, conventional techno-economics assessment models are not able to consider these aspects. This is one of the reasons why in these transitional periods, several of the conservative predictions fail to be correct and determine relevant marked losses in several companies.

Thus, it integrate RES in the chemical production requires major technological and scientific changes, because catalysts, reactors, operations have to be fully redesigned. There are different ways by which RES can be coupled to chemical production: use of electrons (electrical energy produced from renewable sources) in electrocatalytic or non-thermal plasma processes, and use of photons in photocatalytic processes [65]. We omit here to consider instead processes, where concentrated solar power (CSP) is used to heat the reactor, or instead radiations (like microwave) are used for heating the reaction medium. Between photo- and electro-driven processes, we consider the latter closest to industrial exploitation [66], although both are clearly relevant. Their combination in a single photo-electrocatalytic (PEC)

reactor is the basis to develop artificial-leaf type devices in the future [67–69].

Technical hurdles

Electrification has the potential to significantly impact the chemical industry, but some technical hurdles are limiting the actual development, in parallel to the necessary reduction in capital investment and operating costs. Four main technical hurdles can be identified [70].

Increase the "operating flexibility" is still considered a major objective to go in this direction [70]. There are, in fact, fluctuating electricity prices, and furthermore an excess of renewable energy production in some periods (night, for example). It is thus often considered that a requirement is to operate flexibly, i.e. with quick start-up and shutdown times coupled with high efficiencies over varying loads. Current processes instead are designed to operate continuously within a limited range of operation conditions.

A crucial question, however, is that in discontinuous operations, the amortization time is also reduced, and thus CAPEX should be charged on limited times of operations. On the other hand, the continuous decrease in costs in producing renewable electrical energy (REE) indicates that it is preferable to have on-purpose production of REE, which combines with the concept mentioned before of distributed production. We thus believe that this question of discontinuous operations for use of REE in chemical production will be no longer an issue in the near future. On the other hand, there is certainly the interest to use a potential low cost energy, as excess REE during night. Rather than switching off and on the devices, it is preferable to have units specifically designed to operate efficiently with a variable load and thus productivity, i.e. operating, for example, at 50% of full load during day and 100% during night. While current design for chemical plants make them economic only for operations in a very restricted productivity range (typically > 85–90% of maximum capacity), the electrocatalytic operations make possible to operate economically, in principle, with a larger range of capacity. This is an aspect not explored currently, but quite relevant from the implementation perspective.

Extension of operating windows (temperature, pressure) is another relevant challenge [70]. Current commercial electrochemical processes in the area of chemistry are quite limited, essentially adiponitrile synthesis and few minor industrial organic electrosyntheses, in addition to the chlor-alkali process [71]. New large-scale electrolysis units for H_2 production using RES has been also announced. For example, Shell and ITM Power will build the world's largest hydrogen electrolysis plant at Rhineland refinery, Germany, with a peak capacity of 10 MW [72]. However, the development

of technologies and materials to operate over a wider range of operating conditions, will result in new processes and business cases, which are essential factors to increase implementation of the electrification concept.

For example, application of electrocatalytic processes in the area of biomass transformation, as commented later in a more detail, requires to operate in a large range of parameters, such as temperature, pressure and pH, which are relevant to increase the reaction rate and to control the selectivity and stability of operations. Extend the range of operating windows is not only a technological aspect, but requires to design materials and catalysts for stable operations. In addition, engineering of the electrochemical cells has also to be revised, and new simulation procedures for optimization are necessary.

We may consider also two other crucial aspects, which, however, are still not well recognized [66]. The first question is to increase productivity per geometrical area of the electrode. Being capital investment for an electrocatalytic reactor a determining cost element, it is necessary to reduce it by maximizing the ratio between the active electrocatalytic surface and the geometrical electrode surface, i.e. develop what are often indicated as 3D electrode. It must be noted, however, that papers dealing on 3D electrodes refer typically to batteries and analogous devices, or just indicate 3D-like materials, rather than really analyze their use under relevant conditions for electrocatalytic syntheses [73–75].

There are instead specific engineering cell aspects in designing 3D electrodes for chemical syntheses, largely ignored. The first is the realization of a uniform potential distribution of the potential in a nanostructured electrode (especially in large-size electrodes). A non-uniform potential distribution promotes side reactions and influences negatively the selectivity. The second crucial question is the presence of limitations in mass (and in part heat) transport limitations inside 3D porous electrode. In the conventional cell design, where flow rates are limited, these are critical aspects. In addition, diffusion inside a charged porous electrode is different from the case when the potential is not applied. These cell-engineering aspects are generally not considered up to now, or in a very limited extent. They can be instead quite relevant in determining the performances, especially selectivity, when multiple reactions are possible at relatively close applied potential. Examples are in CO_2 hydrogenation or biomass electrocatalytic conversion.

A proper engineering modelling of fluidodynamic in a cell and porous electrode should be developed, accounting also for charge distribution. There are similar problems also in photocatalytic electrodes, where the problem of developing higher productive systems also

exists. Quite few studies exist on the engineering of photocatalytic electrodes [76, 77].

There are several studies on how to develop advanced nanoarchitectures for solar photocatalytic applications [78]. Attention is focused on aspects such as light harvesting, charge-separation, band gap broadening and cocatalysis effects. Low dimensional [12] or hollow [79] nanostructures show several potential advantages for photocatalytic materials, such as enhanced light harvesting, potential reduced charge recombination rate by decreasing charge transfer distance and directing separation of charge carriers, and increased accessible surface areas. This is often masked, however, by an increase in defects, acting as centers for charge recombination. However, the engineering issues in developing photocatalytic electrodes, especially of large size as necessary for industrial applications, are many, and typically not investigated.

For example, the questions of whether there is a homogeneous current density over all the photoanode, of how to improve current collection and of how the interface with electron collecting elements (for example, by introducing carbon nanotubes in an oxide semiconductor) may create local resistances to electron transport. Nanostructure may create local charge accumulation, which can influence light adsorption and charge separation. In addition, there is the question of microfluidodynamics inside a porous semiconductor, with generation of gas bubbles (H_2 or O_2) and presence of a charged surface, with perhaps a not homogeneous surface charge distribution and a liquid (electrolyte) flowing tangential to the surface in pseudo-laminar flow. Other questions regards of how identify the optimal thickness in a nanostructured semiconductor [80], and of how realize an optimal combination between photocurrent generation and transport of protons to a proton-conductive membrane in photoelectrocatalytic devices with compact design [13, 81].

In addition, when a gas is generated by the reaction (for example, O_2 in water oxidation or splitting), there is the problem of bubble formation, which often remain sticked on the electrode, reducing the active surface. This problem is even more critical in nanoporous electrodes, where a gas cap can avoid inside diffusion of the electrolyte.

Therefore, in addition to a proper modelling as a tool for optimization (particularly in scaled-up electrodes), a different reactor design from the conventional ones (typically based on simple electrodes immersed in an electrolyte, or a PEM fuel cell design) is necessary. While the first can be used just for lab testing, the second one (fuel cell) is closer to the design for application. However, this design is not optimal for more complex electrocatalytic reactions than H_2 and O_2 reaction (or the

reverse). In the latter reaction, problems of selectivity are not present and thus it is not crucial to maximize the reaction rate (productivity) at low overpotential.

Extending the use of electrocatalytic technologies to a broader range of reactions of interest for a sustainable chemical production, thus not only requiring broadening of the operating windows, but also to revise completely the electrocatalytic reactor engineering and develop novel optimized flow cells, easy scalable and which minimize the CAPEX costs. Redesign of operations and cells to have an easy (low-energy-intensive) recover of the reaction products under continuous operations has also to be considered. All these aspects are scarcely considered, but it is evident how the push to new technologies deriving from energy and chemistry in transition is opening new perspectives for chemical engineering.

A third critical hurdle [70] is to reduce CAPEX as well as OPEX, working on i) improved electrocatalysts (with higher energy efficiency and stability, but also based on non-critical raw materials), ii) cell and membrane materials, iii) in-situ product separation, and iv) reduction of processing steps. The latter aspect is further discussed later regarding the opportunities in process intensification. Volume production and supply chain development in parallel with increased deployment of electrocatalytic reactors are important aspects in cost reduction, but which cannot be effective without a proper engineering of the systems and the development of suitable mass fabrication methods for components, for example roll to roll techniques for electrodes manufacture. A reduction ranging from 2 to 4, and possibly higher, can be expected, making possible to extend the use of these technologies to a large range of cases.

Electrocatalysis

The core factor limiting often today developments is to identify high efficient and productive electrocatalysts for areas such as electrocatalytic CO_2 reduction and conversion of biomass platform molecules, on which attention is currently focused in the area. EU projects focused on these aspects, especially on the industrial development, are the OCEAN (Oxalic acid from CO_2 using eletrochemistry at demonstration scale; Project ID: 767798), TERRA (Tandem electrocatalytic reactor for energy/resource efficiency and process intensification; Project ID: 677471) and PERFORM (Power platform: establishment of platform infrastructure for highly selective electrochemical conversions; Project ID: 820723), the first two also being coordinated by us.

The word electrocatalysis as opposite to the most common term of electrochemistry should be clarified. They are often considered synonymous [66], but instead understanding their difference is the real challenge facing currently the area.

In fact, an electrocatalyst is not just a catalyst working in the presence of an applied potential, but rather an opportunity to go beyond electrochemistry through catalysis. This is not just a definition, but a concept opening new possibilities still largely underestimated today. For example, when several reactions are possible at quite similar potentials (the case of CO_2 reduction and biomass conversion), based on the electron transfer theory, it is not possible to obtain high Faradaic selectivities to a specific product. The presence of a catalyst, by creating different pathways of conversion, allows combining both higher rate and selectivity. Instead, the rate of electron transfer and reaction depends in conventional electrochemistry on the applied potential, which increase makes possible side reactions, with thus a lowering of the selectivity. Scarcely investigated, however, is how the electrocatalyst active surface changes under application of a potential [82].

While understanding how the catalyst features determine the performances is beginning, using both in-situ/operando methods and theoretical approaches, still many aspects are underestimated. For example, it is known that the electrocatalytic behavior may depend on the facets of the catalyst nanoparticles [83, 84]. However, it is often considered that this is the only aspect determining the reaction paths, for example in CO_2 reduction [85, 86]. On the contrary, we have shown that by changing the effective surface concentration of CO_2 at the electrocatalyst surface, the nature of the products may be considerably influenced. Specifically, products involving C-C bond formation (>C1) theoretically excluded to be possible on the Pt-based electrocatalyst used in these tests, can be instead formed with selectivity of about 60% by using a combination of reactor and electrode design aimed both to increase the effective surface concentration of CO_2 [87]. It was also shown recently that the conventional assumptions in electrokinetic studies (for example, related to Tafel plot) to derive a reaction mechanism in the reduction of CO_2 may not always be valid [88].

Therefore, the methodology used largely up to now was a combination of conventional electrochemistry and catalysis concepts, but not in an integrated approach, which goes beyond and takes advantages from new possibilities given from a broader vision of electrocatalysis required from the new fields addressed. There are still many emerging possibilities, which should be rationalized, in a holistic approach integrated with the engineering of the electrodes and electrocatalytic reactors.

Status in the electrochemical CO_2 reduction

The electrochemical reduction of CO_2 is perhaps the reaction, in the area of electrocatalysis, must intensively studied recently. A large variety of materials has been

investigated, from single-atom catalysts [89], to colloidal nanocrystals [90], metal-organic framework (MOF) materials [91, 92], doped carbon materials [93], gold nanoparticles [94] and manganese-based molecular catalysts [95], just to cite some recent examples of less-conventional type of electrocatalysts.

However, crucial aspects for exploitability, such as productivity, current density, Faradaic efficiency under full loading and stability under practical conditions have been scarcely considered in most of the cases. Electrochemical cells used have typically not considered decisive aspects for development, such as cost-effectiveness, compactness, continuous operations, easy recovery of the products, stability (including by applying full loading) and scalability. New design for the electrocatalytic cells, such as for operations without liquid electrolytes [96], could solve some of these aspects, but have been scarcely considered. Most of the studies are made in conventional cells in the wrong idea that cell engineering is a separate aspect from the development of the electrocatalyst.

A variety of products of CO_2 reduction, going from two-electron reduction as for the production of CO [94] or formic acid/formate [89], to more complex reactions such as the 6 electron reduction to methanol [97] or 8 electron reduction to methane [98], or to even more challenging reactions involving C-C bond formation, such as acetic acid/acetate formation [99] or ethylene and ethanol production [100]. Even the possibility of a selective $18e^-$ reduction of CO_2 to isopropanol was shown [101]. It was often argued that simple reactions (two-electron reduction) should be investigated, for their potential higher productivity and higher Faradaic efficiency. However, this concept is valid, when the electrocatalytic process is considered without its applicative context [66]. Cost of downstream processes, need to realize process intensification and reduction in process steps, minimization of the process steps not using renewable energy sources (compression, thermal catalysis, separation), sustainability, distributed production are some of the elements to evaluate to determine the preferable path. While specific quantitative assessments from this perspective are missing, we would indicate that the preferable directions is towards reactions leading to final products rather than intermediates like syngas. We would also remark that this is another example remarking how the scientific development of the electrocatalysts should be dependent on the engineering assessment of the techno-economic feasibility, an aspect still largely missing in the area of the electrochemical reduction of CO_2. In addition, the technical development has to be put in relation to the strategic vision of the possibilities to create new markets and competitiveness opportunities, as evidenced in the following section.

Creating new value chains

The exploration of above concepts allows to develop innovative value chains. An example is explored in the above cited EU project OCEAN, where the value chain deriving from the possibility to convert electrocatalytically CO_2 with formation of products involving C-C bond formation is explored (Fig. 2). Oxalic acid could be produced either directly by reductive dimerization of CO_2, or via formic acid (or K-formate) electrocatalytic synthesis and further thermal conversion to oxalic acid. From this intermediate, which itself is a chemical with a good market, other products with higher added-value (glyoxylic or glycolic acids), or larger-volume production chemicals such as ethylene glycol, can be produced. These products are actually produced by selective catalytic hydrogenation, but in the future new electrocatalytic processes, with in-situ generation of the H_2-equivalent (H^+ and e^-) necessary for CO_2 reduction, will be possible. In situ water electrolysis or photoelectrolysis could be used to generate the protons/electrons necessary for the reduction of CO_2.
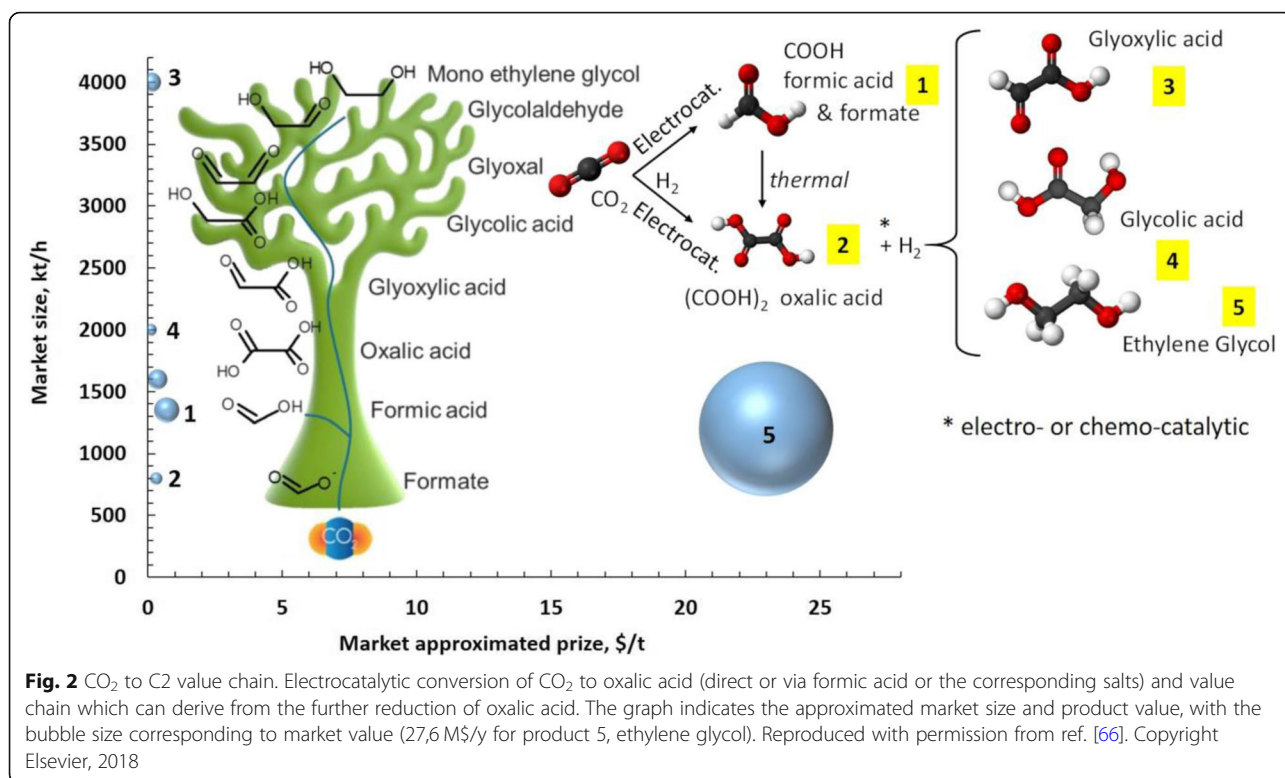
Ethylene glycol is worldwide produced (from ethylene oxide) in over 20 Mt. scale, being used in large-volume polyester fibers and resins. Ethylene glycol is also used in new "renewable" polymers like PEF (polyester polyethylene-furanoate). The production from this route, using CO_2 deriving from biosources (biogas, for example), will allow to produce 100% fossil-free PEF.

Further examples of new value-chains are presented in the next section. In all these cases, which are feasible from an industrial perspective (as explored in the cited EU projects), it is necessary to develop both improved electrocatalysts and novel scalable electro-reactors and units. As commented before, they push chemical reaction engineering to explore new directions, but going beyond the current approaches.

Process intensification

This is an opportunity beginning to be explored [102, 103], being a major change with respect to engineering of conventional plants for chemical production. Process intensification is also a necessary step to move to distributed production.

We refer here only to process intensification related to the use of the electrocatalysis approach, because this is an aspect scarcely considered [66]. There are at least two aspects to mention. The first is the possible relevant reduction in the number of steps and process complexity, which reflects then in lowering the CAPEX/OPEX, the environmental impact and the need to have very large plants. The example illustrated in Table 1 is the difference between the conventional synthesis of ammonia and that possible in an electrocatalytic approach. The actual dominant process of ammonia synthesis

Fig. 2 CO_2 to C2 value chain. Electrocatalytic conversion of CO_2 to oxalic acid (direct or via formic acid or the corresponding salts) and value chain which can derive from the further reduction of oxalic acid. The graph indicates the approximated market size and product value, with the bubble size corresponding to market value (27,6 M$/y for product 5, ethylene glycol). Reproduced with permission from ref. [66]. Copyright Elsevier, 2018

starts from methane as H_2 source and requires several steps to arrive to ammonia. In the electrocatalytic approach (direct synthesis), water is the source of H_2, and thus in a single electrocatalytic reactor N_2 and H_2O are converted to NH_3.

The possible reduction in the carbon foot print is over 90%. There are thus game-charger advantages in this approach: i) large reduction in the process steps, ii) milder operations, iii) elimination of the use of fossil fuels, iv) suitability for distributed production (avoiding impact of large-scale processes and relevant local impact, cost and impact of transporting ammonia), and v) use for the chemical storage of excess renewable energy. While the abundant recent literature focusses essentially only on reaching high Faradaic selectivities (the parallel side reaction is the recombination of protons/electron formed by water electrolysis to give H_2) [104, 105], this is only part of the problem. It is necessary to develop electrocatalysts

based on earth-abundant materials and use flow reactors with easy, non-energy-intensive, recover of ammonia [106], and especially designed to obtain higher productivities per geometrical surface area of the electrode. Most of the data reported in literature for high Faradaic efficiency were obtained at extremely low productivities, or current densities. There are other issues, however, which have been not considered up to now. The current industrial ammonia synthesis technology starting from methane uses air as N_2 source, because the oxygen is then consumed in the process.

In the direct electrocatalytic approach, pure N_2 has to be fed, because otherwise oxygen recombines with protons/electrons at the cathode side to form water. A membrane for N_2 and O_2 separation should be integrated with the electrocatalytic unit, but still some residual oxygen will be present. Therefore, the challenge (not considered up to now) is how to develop electrocatalysts for ammonia

Table 1 Comparison of the actual industrial production of ammonia versus the direct electrocatalytic route. Reproduced with permission from ref. [66]. Copyright Elsevier, 2018

Production	Description	Total C-footprint[a]
Actual industrial	Multistep and high pressure/temperature process, starting from natural gas. *Steps:* purification, steam reforming, air reforming, shift converter, CO_2 removal, methanation, compression/cooling, NH_3 synthesis, cooling/decompression. Efficient only in large-scale (transport, impact).	1.83 t_{CO2}/t_{NH3}
Direct electro-catalytic	*One-single device* (suited for distributed production). Start from N_2, H_2O and renewable energy, nearly room temperature and ambient pressure.	0.12 t_{CO2eq}/t_{NH3} (93% reduction)

[a]from ref. [5]

synthesis (from N_2 and H_2O) operating efficiently in the presence of some residual O_2 after air separation. The problem is thus significantly different from current studies on the reaction [107–109], where the only issue considered is a high Faradaic selectivity to NH_3.

The problem of oxygen contamination, the recovery of ammonia and flow reactor operations, the design to minimize ammonia crossover through the membrane [110], a compact scalable reactor design, the use of low-cost scalable synthesis of electrocatalysts, stability under operation are some of the problems to consider from an engineering perspective, which are not separated from the development of the electrocatalysts, and may instead determine different selections, as remarked before for water splitting catalysts.

Another relevant example of possible significant reduction in the process steps, and carbon footprint, is given by the direct electrocatalytic synthesis of acetic acid or acetate from CO_2 [99, 111–113]. Acetic acid is also a large-volume chemical (about 14 Mt. annually) with a market in expansion. Current production routes use fossil sources, apart from few based on fermentation processes. The current main industrial route is a multi-step process, via production of syngas from methane, production of methanol, and carbonylation of the latter. The overall energy efficiency is about 15%, which can significantly increase in direct electrocatalytic routes, with also a reduction of the carbon footprint over 50%. The key aspect is also in this case how to control selectivity and favor reactions leading to C-C bond formation [99], but considering that often mechanistic studies provide contrasting results, because they do not consider the role of surface coverage (or reactants and products, electrolyte) in determining the paths of electrocatalytic transformations [87, 113], the use of different reactor configurations (in the presence or not of an electrolyte of support [114]), and the dependence on the potential applied [82].

There are thus several fundamental open questions to understand, but requiring a broader approach than the limited often currently used. A closer relationship between fundamental and applied/engineering aspects is necessary. On the other hand, new value chains and opportunities will derive from these studies.

A second and different possibility for process intensification is related to the application of the electrocatalytic approach to the production of chemicals from biosources. Here the point is that in these processes, both catalytic oxidation and reduction steps are often present. They can be conveniently joined in a single tandem or paired electrocatalytic reactor, as explored in the previously cited EU TERRA and PERFORM projects.

The specific business case, and tandem electrocatalytic reactor, explored in the TERRA project regards the synthesis of PEF, a novel biobased polymer which should substitute polyethylene-terephthalate (PET), a major polymer (> 20Mt production).

PEF is synthetized by co-polymerization of FDCA (2,5-furandicarboxylic acid) with ethylene glycol. Avantium e BASF created two year ago the joint venture Synvina to construct a new plant (50,000 t/y) for the production of this polymer. FDCA derives from fructose as raw materials via intermediate HMF formation, while ethylene glycol still derives from fossil sources (via ethylene and ethylene oxide). The production of ethylene glycol from biobased byproducts such as xylose, as in the case discussed before from bioderived CO_2, could thus produce 100% bioderived PEF. Interesting is that the two monomers for PEF could be synthetized one by oxidation and one by reduction of platform biomolecules (HMF and xylose) deriving from cellulose and hemicellulose, the main components of biomass.

TERRA project thus explores the development and scale-up of a tandem electrocatalytic reactor, schematically shown in Fig. 3, where the two monomers (FDCA and ethylene glycol) are produced in the same reactor. The approach avoids the need of oxidizing and reducing agents for the two redox reactions and the process intensification decreases the process steps and allow better energetic integrations. The result is a decrease of CAPEX and OPEX by more than 20%. There are, on the other hand, a series of technological aspects to solve, besides to develop the electrocatalysts allowing high selectivity and stability.

One of the crucial issues is the fact that the optimal temperature of operation could be not the same for the two sides of the electrocatalytic reactor. Inside the TERRA project, a technological solution to decouple the temperature of the two sides of the reaction (within a certain range) has been developed, although cannot be discussed in detail here. This is a new innovation aspect not present in conventional electrochemical approaches, but opening a range of new possibilities in coupling redox reactions.

Moreover it represent an example of how the need to solve critical questions from the application side pushes the development of new engineering solutions, which, on the other hand, open new fields of application.
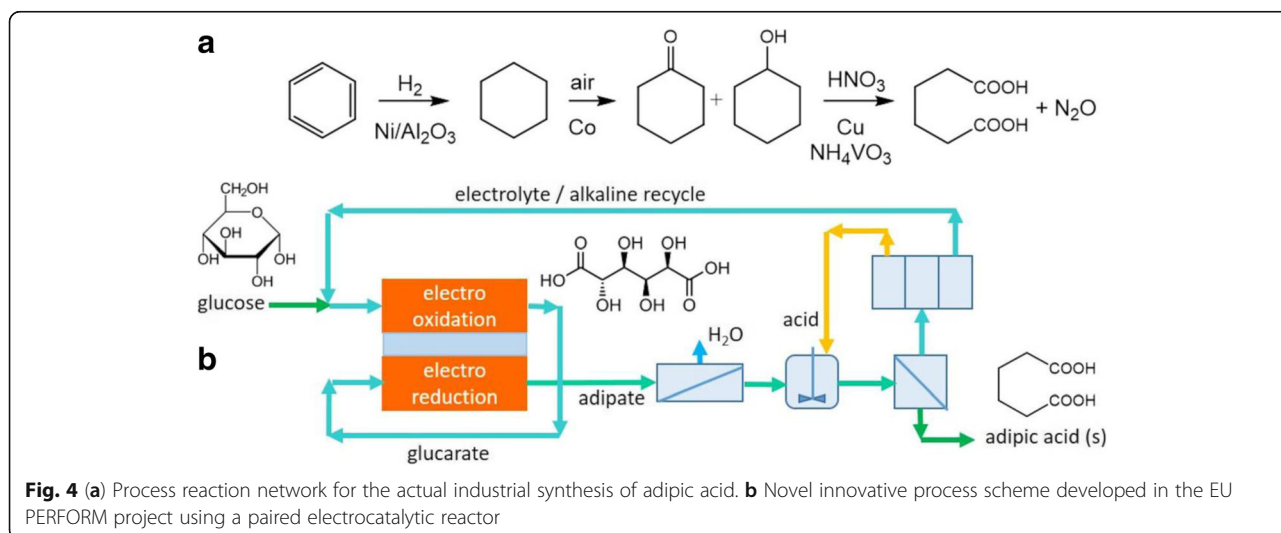
In fact, a range of new possibilities opens in the area of biomass valorization using electrocatalytic approaches. Some of them are explored in the cited PERFORM project. An interesting example is that coupled redox reactions are present in the synthesis of other biobased monomers such as adipic acid, one of the most important of the commercially available aliphatic dicarboxylic acids [17, 115]. A major route for its industrial production is based on the hydrogenation of benzene to cyclohexane, which is then oxidized to a mixture of cyclohexanol and cyclohexanone (indicated as KA oil).

Fig. 3 Innovative intensified electrochemical process developed in the EU TERRA project
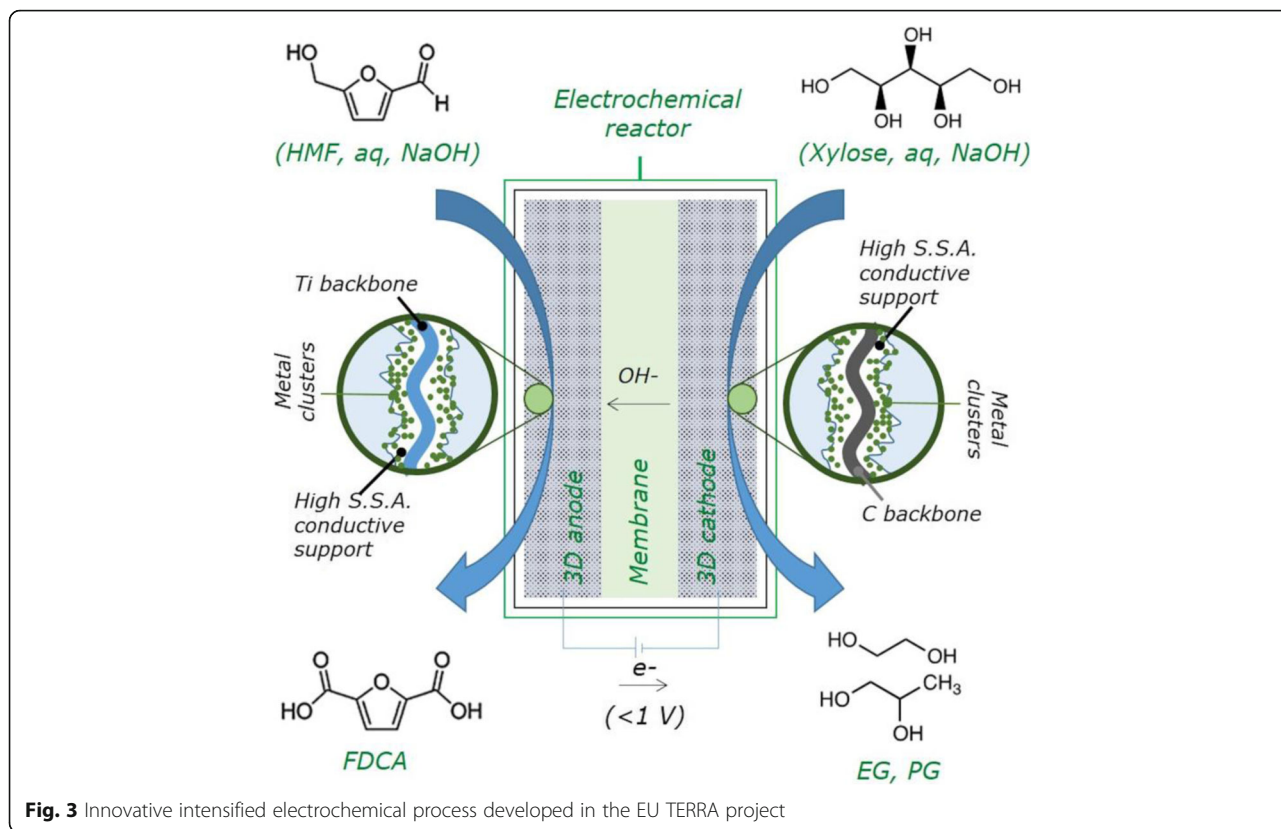
KA oil is then oxidized with nitric acid producing N_2O as byproduct, a powerful greenhouse gas (Fig. 4a). The full process thus involves many steps, uses toxic chemicals (benzene), produces N_2O as byproduct, and requires both reducing agents (H_2) and oxidants (O_2, HNO_3). The new electrocatalytic process starts from a safer raw material (glucose) and uses a single electrocatalytic reactor, with a relatively simple downstream separation. The entire process, avoiding the use of reductants and oxidants,

significantly decreases the carbon footprint, greenhouse gas emissions and the environmental impact. In addition, the process is well suited for distributed production allowing thus to develop novel business models.

There are many novel electrocatalytic, reactor engineering and process technology aspects to develop for enabling the implementation of the process, but which can open novel market opportunities for various other applications.

Fig. 4 (**a**) Process reaction network for the actual industrial synthesis of adipic acid. **b** Novel innovative process scheme developed in the EU PERFORM project using a paired electrocatalytic reactor

Conclusions

Many aspects, from economic to sustainability, social and political, are inducing a radical transition in both the energy and chemical production systems. This creates a push for new chemical reaction technologies and associated engineering aspects. We have identified in this review two main aspects on which focus the discussion: i) the development of alternative carbon sources and ii) the integration of renewable energy in the chemical production. These areas cannot be considered just an extension of the current ones. Therefore, they should be properly addressed by developing new tools for chemical engineering assessment, in parallel to innovative methodologies for development of the materials, reactors and processes needed to enable from the technological side the realization of the necessary targets in an integrated fundamental and applied/engineering vision. Often these aspects are still underestimated. Some R&D aspects are highlighted, to remark that they are crucial elements to accelerate transition to a more sustainable use of energy and chemistry. Moving in the indicated directions will produce radical changes in the way production is made, requiring thus new fundamentals and applied engineering approaches.

In conclusion, we hope to have demonstrated that exists a push for new chemical reaction technologies deriving from energy and chemistry in transition. However, the speed to which this transition will be enabled will also depend on the capability to have a broader and integrated view on the problems. Some of the needs have been discussed here.

Abbreviations
CAPEX: Capital expenditure; COTC: Crude-to-chemicals; CSP: Concentrated solar power; FDCA: Furandicarboxylic acid; HMF: Hydroxymethylfuran; HT: High temperature; MSW: Municipal solid waste; OCM: Oxidative coupling of methane; OPEX: Operating expenses; PEC: Photo-electrocatalytic; PEF: Polyester polyethylene-furanoate; PEM: Proton-exchange membrane; PET: Polyethylene-terephthalate; RdF: Refuse-derived fuel; REE: Renewable electrical energy; REE: Renewable energy sources; WtC: Waste-to-chemicals

Authors' contributions
CG, GI and SP have made substantial and equal contributions to the conception of the manuscript and have approved the submitted version. They agreed both to be personally accountable for the author's own contributions and to ensure that questions related to the accuracy or integrity of any part of the work are appropriately investigated, resolved, and the resolution documented in the literature. All authors read and approved the final manuscript.

Ethics approval and consent to participate
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