

Catalysis for biomass and CO₂ use through solar energy: opening new scenarios for a sustainable and low-carbon chemical production†

Cite this: *Chem. Soc. Rev.*, 2014, 43, 7562

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The use of biomass, bio-waste and CO₂ derived raw materials, the latter synthesized using H₂ produced using renewable energy sources, opens new scenarios to develop a sustainable and low carbon chemical production, particularly in regions such as Europe lacking in other resources. This tutorial review discusses first this new scenario with the aim to point out, between the different possible options, those more relevant to enable this new future scenario for the chemical production, commenting in particular the different drivers (economic, technological and strategic, environmental and sustainability and socio-political) which guide the selection. The case of the use of non-fossil fuel based raw materials for the sustainable production of light olefins is discussed in more detail, but the production of other olefins and polyolefins, of drop-in intermediates and other platform molecules are also analysed. The final part discusses the role of catalysis in establishing this new scenario, summarizing the development of catalysts with respect to industrial targets, for (i) the production of light olefins by catalytic dehydration of ethanol and by CO₂ conversion via FTO process, (ii) the catalytic synthesis of butadiene from ethanol, butanol and butanediols, and (iii) the catalytic synthesis of HMF and its conversion to 2,5-FDCA, adipic acid, caprolactam and 1,6-hexanediol.

Received 3rd November 2013

DOI: 10.1039/c3cs60396b

www.rsc.org/csr

Key learning points

- (1) How the use of raw materials as alternative to fossil fuels opens new scenarios for a sustainable and low carbon chemical production.
- (2) The role of CO₂ reuse to introduce renewable (solar) energy into the chemical production value chain.
- (3) How to assess using multiparameter criteria the most relevant routes to enable a new sustainable future for chemical production.
- (4) The role of catalysis and the open issues in establishing this new scenario, with reference to three selected relevant cases.

1. Introduction

Many indications, from socio-economic to technological, point out that the chemical industry is moving to a new development cycle. This is characterized by global structural changes in the economy with a crucial reorganisation of the energy and resource infrastructure, in which the switch to renewable energies and sustainable issues is largely influencing the market and industrial objectives.^{1,2a} The efficiency and use of renewable resources and energy, particularly in geographical regions poor of natural resources such as Europe, is becoming a

driving element for competitiveness and strategies in the chemical and process industry. The use of alternative “green/sustainable and renewable” resources such as biomass and solar energy for the development of new solutions to produce raw materials and energy vectors is thus becoming an industrial priority.

Catalysis is a key enabling factor to allow the development of new sustainable processes and technologies and thus plays a critical role to realize this transition.² Consequently, the development of catalysts and related catalytic technologies for the use of (i) biomass to produce chemicals and fuels, and (ii) renewable energy in chemical production is becoming a key area of the research. For the latter, we should clarify that the direct use of solar energy in photochemical organic syntheses is an area of minor interest from an industrial perspective (although potentially attractive) for the (still) low productivity/selectivity, while there is a growing interest in the use of

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† Part of the catalysis for production of renewable energy themed issue.

renewable (solar) energy for producing H₂ and converting CO₂, either directly (photochemically) or indirectly. The latter refers to the use of the electrical energy generated by solar energy (photovoltaic, concentrated solar power – CSP, *etc.*) or of other related renewable energy (RE) sources (such as wind and hydro) to produce H₂ (used then to convert catalytically CO₂) or directly to convert (electro-catalytically) carbon dioxide. We refer here to this direct and indirect use of renewable (solar) energy for converting CO₂ when discussing this topic.

Many recent reviews have discussed these topics recently. A limited selection is represented by the reviews of Dumesic *et al.*,³ Kobayashi and Fukuoka,⁴ Corma *et al.*,⁵ Miertus *et al.*,⁶ Stocker,⁷ Rinaldi and Schüth,⁸ and Gallezot⁹ on different aspects of the catalytic chemistry in biomass conversion to chemicals and fuels, and the reviews of DuBois *et al.*,¹⁰ Centi *et al.*,¹¹ Quadrelli *et al.*,¹² Aresta and Dibenedetto,¹³

Sakakura *et al.*,¹⁴ Wang *et al.*,¹⁵ and Leitner *et al.*¹⁶ on different aspects of the catalytic chemistry of CO₂ utilization. Several books have also been published on these topics, amongst which may be cited those of Triantafyllidis *et al.*¹⁷ on the role of catalysis for the sustainable conversion of biomass and of Aresta¹⁸ on the use of CO₂ as a chemical feedstock.

The discussion on CO₂ catalytic chemistry, however, has been mainly centred on the use of CO₂, with limited aspects regarding the issue of incorporation of RE into the cycle of CO₂ conversion, particularly from an industrial perspective.^{11b} Being carbon dioxide low on the thermodynamic energy scale, a sustainable use of CO₂ requires the energy to proceed uphill to the product of reactions (typically at a higher energy level than that of carbon dioxide) is provided by RE sources, directly (as photons, electrons) or indirectly, *via* high-energy molecules such as H₂ produced with the use of RE.

This concept is presented in Fig. 1. CO₂ could be converted to inorganic carbonate in an exo-energetic path or to organic carbonate (as example for the various routes to form CO₂-containing polymers or organic chemicals) by reaction with a high-energy molecule (ethene oxide in the example of Fig. 1). However, these routes do not incorporate RE in the process of carbon dioxide conversion. On the contrary, both direct routes of conversion of CO₂ using electrons produced using RE sources (electro-catalysis) or using photons (photo-catalysis), and indirect routes in which renewable H₂ (produced using RE sources) is first produced, and then this hydrogen is utilized in the catalytic processes of CO₂ conversion (to form CH₃OH, CH₄ or CO, for example) lead to incorporation of RE into the final product.^{11b}

The direct route of conversion of CO₂ using photons (photo-catalysis) is apparently the more challenging and interesting. Various specific reviews have been published on the photo-conversion of CO₂ on semiconductor materials, for example by Mao *et al.*,¹⁹ Habisreutinger *et al.*,²⁰ Garcia *et al.*²¹ and Fan *et al.*²² In this case, the mechanism of light capture and energy



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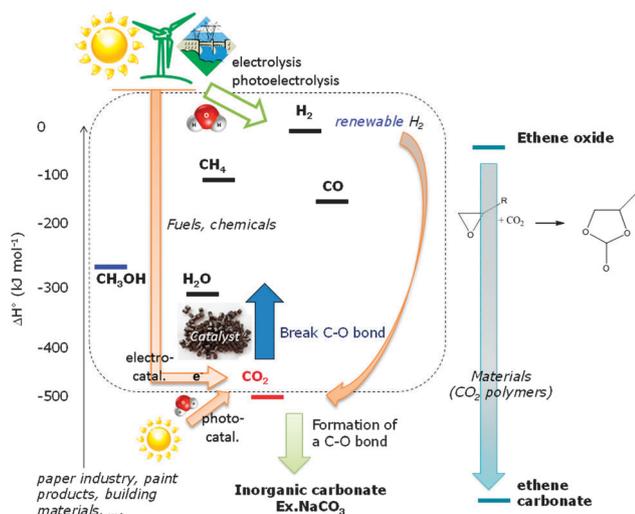


Fig. 1 Energy scale in some of the products of CO₂ conversion, illustrating the different routes by which RE could be introduced in the carbon dioxide molecule to produce fuels or chemicals.

transfer to a CO₂ molecule has been discussed, but the productivity is still too far from those necessary for exploitation (needing a three order of magnitude intensification). Industrialization still appears unrealistic, even taking into account the possible developments in the semiconductor materials. While typical aspects are discussed regarding the need of cocatalysts, the interfacial contact between semiconductor and other materials as well as the role of heterojunctions in promoting charge separation, and the design strategy in semiconductors to improve effectiveness in using the visible light portion of the solar spectrum, there are many aspects regarding the interaction of CO₂ and of the products of conversion with surface excited states which have been scarcely investigated.^{2,3} The analysis of these aspects suggest the presence of intrinsic barriers to increase productivity in CO₂ direct photoconversion to the levels necessary for exploitation.

Also in the case of biomass conversion, the issue of the energy use in the production of the final products is often not analysed to evaluate the different possible paths, although in this case the analysis is more difficult and should consider the full cycle of production on a LCA (life-cycle assessment) basis.

2. Scenario analysis for a sustainable and low-carbon chemical production

Current chemical production, limiting discussion here to petrochemistry, is mainly oil-centric (>90%) and based on the use of a few building blocks (light olefins, aromatics, few alkanes such as *n*-butane, and syngas). Other fossil fuel feedstocks still have limited use. Methane is used essentially to produce H₂ and syngas, the latter mainly used to produce methanol – about 65 Mt per year – and related value chain. Other alkanes present in natural gas (NG), such as ethane and propane, are used for the production of light olefins by steam

cracking or direct dehydrogenation. Coal still finds limited usage for chemical production, even though its use to produce syngas converted then to methanol and finally light olefins is considerably promoted in China.

Shale gas is expected to change this panorama, due to the increased availability of low cost NG promoting an increased use also in chemical production. Several chemical companies are looking to the new opportunities created by shale gas to expand production capacity for ethylene, ethylene derivatives (*i.e.*, polyethylene, polyvinyl chloride, *etc.*), ammonia, methanol, propylene, and chlorine. However, this situation cannot be generalized, particularly for geographical areas such as Europe where shale gas production will be limited due to the large environmental concerns.

Consequently, we may forecast that world chemical production will progressively move from an oil-centric common vision to different regional-based systems. US will promote chemical production centred on the use of shale-gas, China that based on coal utilization and the Middle East that based on oil use, due to the low local costs. For Europe, to remain competitive in this global competition, it needs to foster the use of alternative raw materials. The possibility for European chemical production, to remain competitive in this evolving scenario of raw materials, is to foster the use of its own resources, biomass (particularly, waste) and CO₂. The central role of these two raw materials in redefining the future scenario of chemical industry is recognized from important actions of the European chemical industry, such as the public-private partnership SPIRE (Sustainable Process Industry through Resource and Energy Efficiency).

We limit the discussion here, for conciseness, to the development of a sustainable and low-carbon chemical production, *e.g.* based on the use of biomass and CO₂, the latter through the use of renewable (solar) energy. As briefly mentioned above, this is a priority especially in Europe, but different geographical areas may have different priorities, particularly the use of shale gas in the US and coal in China. Although the chemical industry (and trade) is currently highly globalized, there is an evolution towards a deglobalization with a tendency to use and value local resources. The model of globalization of chemical production has shown its limits, and various economists have evidenced the role of the globalization approach in the current global crisis, often contrasted with governmental stimulus programs meant to rev up national markets. In the deglobalization approach,²⁴ production for the domestic market must again become the center of gravity of the economy rather than production for export markets. With respect to similar trends occurring at the beginning of the last century in response to the Great Depression, this time the “domestic” market is seen as an area market (Europe, for example, instead that limited to single European countries), and a larger social pressure exists (in terms of equitable income redistribution, deemphasizing growth to empower upgrading the quality of life and environmental preservation).

This change in approach also influences the priorities for chemical production moving beyond the key criterion of reduction of unit cost, to consider the integration in the social and environment value chain. Industrial and trade policies will

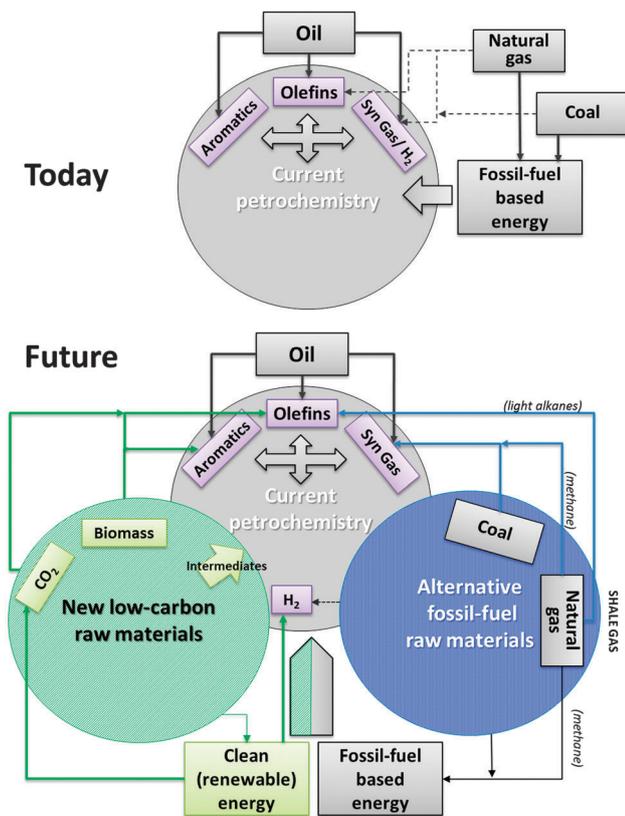


Fig. 2 Evolution in the scenario of raw materials from current petrochemistry to the future scenario for a sustainable and low carbon chemical production.

be the driving element for this change, which reflect also in a change in future raw materials for chemical production. This is schematically shown in Fig. 2.

Moving to the use of alternative fossil fuel raw materials will be driven from economic (shale gas, in US) and in part geopolitical (coal, in China) motivations. Although the increasing production trend of shale (or “tight”) gas in the US has generated a wave of optimism, the actual EIA (US Energy Information Administration) data show that the total US gas production has not been growing for the past 1–2 years and that signs of decline are instead present. Drilling rigs for gas have been plummeting over the last two years. These data seem to confirm the interpretation of a financial “gas bubble”, rather than a robust trend of development of new resources. In the near future, the decline in gas production in the US may lead to an increase in prices. In addition to these uncertainty about future shale gas costs, the environmental burdens (methane fugitive emissions; volumes of water and the chemicals used in fracking and their subsequent disposal; risk related to contaminating groundwater due to shale gas extraction; competing land-use requirements in densely populated areas; the physical effects of fracking in the form of increased seismic activity, *etc.*) have to be accounted for. For these reasons, shale gas use for chemical production is reasonably unrealistic in various areas of the world. As briefly outlined in Fig. 2, the contribution of shale gas to the future scenario is confined to (i) additional

methane available for syngas/H₂ production or energetic uses associated to chemical industry, and (ii) additional light alkanes available for light olefins production (particularly, by steam reforming and to a lesser extent by dehydrogenation).

A different situation is present on the use of coal for chemical production in China, with motivations often being mixed with geopolitical reasons, and economics difficult to translate to different countries. Coal is essentially usable for chemical production only *via* the methanol/olefin route, except for some possible contribution to the energy needs of chemical industry.

It is thus clear that the relative weights of the three areas indicated in Fig. 2 (bottom) to the future scenario of chemical production will be different in different geographical areas and not easy to predict. We could note, however, that the use of new low-carbon raw materials (biomass, particularly biowaste, and CO₂/renewable energy) shows a better impact in terms of a (i) sustainable and low carbon economy, (ii) balanced use of local resources (integrated biorefineries) and synergy with other economic activities (agriculture and forestry, especially) and (iii) integration within the chemical production value chain (production of intermediates and high-added-value products, in addition to base raw materials).

The availability of these raw materials (biomass, CO₂) is clearly an important element for the evaluation of the effective impact of these routes. In 2010, the European chemicals industry, including pharmaceuticals, used a total of 54 million tonnes of oil equivalent (MTOE) of fuel and power consumption. The total biomass potential for EU27 (calibrated studies, *e.g.* compensated for geographical differences and biomass categories, for 2020–2030 decade) is between 4–20 EJ per year (96–478 MTOE), of which between 20 and 50% (depending on estimations) are derived from agricultural residues and organic biowaste, the remaining from energy crops, forestry and forestry residues. Considering 30% as the target for biomass substitution of fossil fuels in EU27 chemical production in year 2030, and 50% as the average yield to chemicals in converting biomass, the amount of available agricultural residues and organic biowaste is in excess to that necessary to cover the needs.

According to the European Environmental Agency (EEA), the European chemicals industry, including pharmaceuticals, emitted in 2010 a total of 166 million tonnes of CO₂ equivalent (down from a total of 330 million tonnes in 1990). Of these emissions, over 20% are easily recoverable. Many large-volume sources of rather pure CO₂ in refinery and chemical processes (ammonia production, ethylene oxide production, gas processing, H₂ production, liquefied natural gas, Fischer–Tropsch – synthesis) as well as from biorefineries (ethanol production) exist. The amount of CO₂ which could be easily recovered from chemical production alone could potentially account for about half of the light olefin production in EU27, while a reasonable target for year 2030 is about 10–15%.

Therefore, this brief analysis evidences how the availability of biowaste/agricultural residues and CO₂ will not be the limiting factor to develop a sustainable low-carbon chemical production in the next two decades. This statement is valid also for

other geographical areas, such as Asia, US *etc.* where the degree of penetration of biowaste and CO₂ as alternative raw materials will be even lower than in Europe, as discussed before.

2.1 Selecting the future paths based on the use of biomass and solar energy

Sustainability is a major driver for the future scenario of the chemical industry,¹ but many other factors (internal to chemical industry, such as process economics, availability of raw materials, company strategies and synergies, *etc.*, and external, for example, limitation on greenhouse gas emissions, environmental regulations, company visibility, *etc.*) determine the possibility that a potential route (technically feasible) becomes effectively a major industrial route.

This review, different from the others cited before as well as the many others present in the literature, will first analyse the future scenario of the chemical industry, in order to select the main routes having the possibility to become relevant production routes alternative to those actually in production (based mainly on the use of fossil fuels). The criteria for this selection are the following:^{2a}

– *Economic drivers (ED)*. An important initial element for evaluation is whether the economic bases for the switch to new raw materials exist. We refer here only to considerations about estimations of raw material cost and product value (projection to future values), as well incidence of fixed costs based on the process complexity (in particular, regarding purification of both raw materials and products of reaction). It is thus limited to estimate when an economic potential exists to industrialize the process. The cost of production depends on many factors, which have also a large variability from country to country and company to company as well. In addition, estimation of process economics requires to have established in detail the process flowsheet, but this contrasts with a scenario analysis on processes often at an early stage of development. Therefore, evaluation should be limited to considering whether an economic potential to industrialize the process, and clear economic drivers to push the technological development of the process, exist.

There are also other important components in the evaluation of the economic drivers. Between these, the investment cost necessary to develop the process and the integration of the production within the existing infrastructure (drop-in products). In a rather uncertain future scenario of energy and raw material costs, processes requiring large investments, rather long (>10 years) amortization times, and which not well integrate within the existing production infrastructure and value chain have lower possibilities to become major production routes.

– *Technological and strategic drivers (TSD)*. The scenario for the chemical production in the last half century was capital intensive, reflecting the large manufacturing facilities required to produce bulk quantities. This has given the industry a competitive advantage in terms of high barriers to entry, but the fast development in areas with low production cost such as Asia and globalization has broken down this model. Knowledge-based and high technology production is a major current driver for competitiveness.

The development of new production routes based on alternative raw materials, particularly when using low-cost raw materials such as waste biomass and CO₂, offers clear incentives from this perspective, particularly for industrial newcomers that need to establish their business area. Time to market for these new players, however, is an important component of the possibility to success. The traditional approach based on lab-bench-pilot-demo sequence is time consuming. New models of production, based, for example, on parallel modules^{2a} could reduce largely this time, bypass the scale-factor approach determining the industrial choices in the last half century, and could allow operating at full capacity of utilization even in the presence of a fluctuating market. An example is given from the results of the F3 (Fast, Future, Flexible)-Factory EU project, where major EU companies are collaborating to develop this new production model.

In terms of drivers for establishing new production routes, the possibility of a fast time to market, which is related to both the possibility to exploit new production approaches and to the presence of technologies not requiring costly development are relevant elements for the evaluation. Other elements such as flexibility of operations and capacity utilization rates are also important, as well as the innovation character of the process creating knowledge-based barriers to competitiveness rather than on other aspects.

Process complexity index is an aspect in part related to those discussed above, and which is another relevant aspect to consider in evaluating the possible scenario for the future chemical production. A reduced number of process and separation steps, simple separation units, high productivity and reduced number of byproducts, limited need of special materials and safety measures/devices are important elements determining the possibility of success for new production routes.

Between the strategic drivers, it must also be considered the trend towards a de-globalization of the chemical production. There is a need to realize stronger synergies with downstream industries and user, as well as symbiosis with other productions on a regional basis. This is the clear trend observed in biorefineries.²⁵ The need to use local biomass resources, of their full utilization to produce also high-added value products (integrated chemical and energy production), the necessary strong link with the territory are all elements driving towards new models of biorefineries (with respect to the traditional ones), with clear relevant impact also on the future routes of chemical production.

– *Environmental and sustainability drivers (ESD)*. The efficiency in using energy, resources and in limiting the impact on the environment are elements of increasing relevance for the chemicals industry and to determine the successful rate of new chemical productions. The efficiency includes the possibility of symbiosis with other productions.

However, a careful analysis has to be made, based on LCA or related methodologies. The use of biomass as raw material, for example, does not imply that a process shows a better sustainability than the analogous based on the use of fossil fuels. Often only using waste biomass the process shows a lower impact on the environment. On the other hand, it has to

remark that the application of LCA methodology to a chemical process shows still several limits, both in terms of a lack of reliable data for the analysis, and in terms of categories of analysis that do not well adapt to evaluate the chemical production.

It is also important to remark that still many of the actual chemical production routes (based on fossil fuels) suffer from significant drawbacks.²⁶ If we consider a combined parameter of efficiency reflecting both the feed efficiency (C lost per C built into the product) and the energy efficiency (C lost per C built into the product, after converting the consumption of fuel, power and steam into methane equivalent), there are various processes showing a high value of this parameter (higher than about 1), for example: (i) cyclohexane to caprolactam, (ii) adipic acid synthesis from benzene, (iii) methane to HCN and to NH₃, (iv) dinitrotoluene to toluene diisocyanate, (v) methanol to dimethylcarbonate, *etc.* There are also still many processes with a high inorganic waste production, for example (a) toluene to dinitrotoluene, (b) acetone to methyl-methacrylate, (c) cyclohexane to caprolactam, and (d) propylene to epichloridrin. Integration of the manufacturing line up to the final polymer (from raw materials) is also important.

Most efficient processes are those for polyolefins and polystyrene. Energy-consuming routes are the production of PVC (polyvinyl chloride) and Nylons, and large amounts of wastes are produced in Nylon, PMMA (polymethyl-methacrylate), polyurethanes, epoxy resins, and polycarbonates processes. The sustainability of these routes does not imply necessarily the use of alternative raw materials to fossil fuels, but can be a possibility to reduce the environmental impact.

– *Socio-political drivers (SPD)*. There is low public esteem for the chemicals industry. Public opinion must not be underestimated – it can be a powerful ‘driver’ of the business environment. In addition, public opinion can act as a strong catalyst for regulatory initiatives, which do not necessarily create a favourable business environment. Therefore, socio-political visibility of the different routes is an element for their possible success.

Establishing the possible routes for the future scenario of the chemical industry will thus require a multifactor evaluation. Several of the discussed aspects cannot be fully quantified, at least in a scenario analysis where several of the elements necessary for the evaluation are missing. Scenario analyses thus contain some arbitrary elements that may be questioned. Nevertheless, it is a useful exercise, particularly in a tutorial review, to discriminate between the many possible routes in using biomass and solar energy (the latter, through CO₂ conversion) which can confuse researchers approaching this field. The aim of this introductory scenario analysis is thus to pose the discussion of the status of the development of the catalysts in these different selected routes on more solid bases.

2.2 Defining the new scenario for a sustainable and low carbon chemical production

In a recent paper dedicated to the challenge of introducing green energy in the chemical production chain¹ we have anticipated a possible new scenario for a sustainable chemical

production based on the reuse of CO₂ and of biomass to produce both raw materials (building blocks) and specific intermediates, even though discussion was limited to a few aspects of CO₂ reuse. Fig. 3 illustrates schematically the concept of how CO₂ as a carbon-source in integration with platform molecules derived from biomass, and lignin to produce aromatics, make it potentially possible to avoid the use of fossil fuels for chemical production (limited to organic products).

In a more realistic target, about 30% of the use of fossil fuels (in year 2030) could be substituted by use of biomass, CO₂ and renewable energy (for the part concerning the use of fossil fuels as energy vector). This is the target of the cited SPIRE initiative promoted by the European Chemical Industry Council (Cefic) and thus shared by many chemical companies at least for the European scenario (which covers about one third of the chemical production worldwide). This percentage of 30% is expected to increase further in subsequent years, an objective which can be reached even with a faster rate. History teaches us that about six decades ago, the introduction of olefins as alternative raw materials to acetylene and other chemicals led in about two decades to a complete change in the chemical production. There are many aspects indicating the existence of a similar situation that may lead to a fast transition to the new scenario for chemical production. It is thus important and relevant to prepare this transition and highlight the routes having the higher possibilities to become major future routes of chemical production.

Fig. 3 does not include the use of alternative fossil fuels (coal and shale gas, see Fig. 2), because it is focused on new low-carbon raw materials. At the beginning of this Section 2 the possible role of these alternative raw materials in a future scenario has been discussed, but from a sustainability and low-carbon economy perspective both these raw materials show significant drawbacks. This is especially true for coal, due to the high impact on the environment associated with the production and use of coal.

Another note regards the fact that only some main routes can be discussed here to focus the discussion. The aim is to provide some relevant examples, rather than a systematic and complete analysis of all the possibilities and new routes, not compatible with the objectives of a tutorial review.

2.2.1. Novel sustainable light olefin production routes. Light olefins (ethylene and propylene) are produced worldwide in an amount of about 200 Mtons per year. Their synthesis is the single most energy-consuming process in the chemical industry. The largest part of ethylene and propylene is used to produce polymers by direct routes (polyethylene and polypropylene; polypropylene production, for example, accounts for more than 60% of the total world propylene consumption) or by indirect routes. For example, the main products of propylene conversion (acrylonitrile, propylene-oxide, acrylic acid and cumene) are also mainly used to produce polymers (see Fig. 3).

Currently, light olefins are produced principally by steam cracking and this process accounts for about 3×10^{18} J of primary energy use, not counting the energy content of the products. The pyrolysis section of a naphtha steam cracker

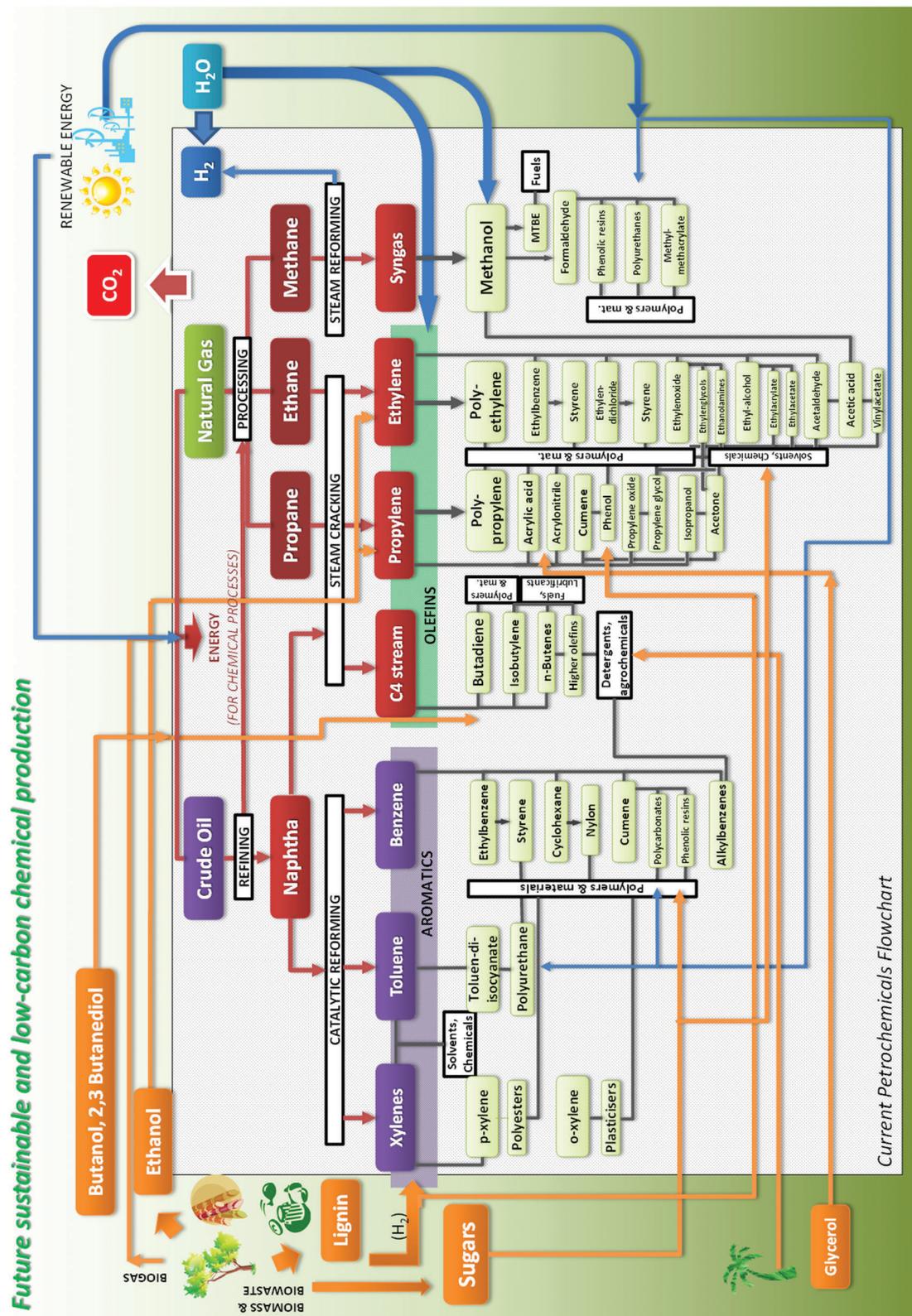


Fig. 3 Simplified flowchart of current petrochemical production with an outline of the possible new scenario for a sustainable chemical production based on the reuse of CO₂ and of biomass to produce both raw materials (building blocks) and specific intermediates. Modified from ref. 1, © 2014.

alone consumes approximately 65% of the total process energy and accounts for approximately 75% of the total energy loss.

The specific emission factor (CO₂ Mt/Mt light olefin) depends on the starting feedstock, but ranges between 1.2 and 1.8.

About 300 Mtons per year of CO₂ derive from the production of these building blocks of the chemical production chain.

Light olefins can be produced from different sources (crude oil, natural gas, coal, biomass and bio-waste such as recycled plastics, and CO₂),^{27,28} as summarized in Fig. 4. The main current processes (indicated with bold black arrows in Fig. 4) are the steam cracking of oil and NG fractions, with minor production by direct dehydrogenation of alkanes. Olefins are also a side product of the fluid catalytic cracking (FCC) process in the refinery, but are usually utilized inside the refinery for alkylation or oligomerization processes.

New process routes, already at an industrial level, include the dehydration of ethanol produced from biomass fermentation and the production *via* syngas (through the intermediate synthesis of methanol), with the syngas deriving from coal combustion or biomass pyrolysis/gasification. Methanol can be converted to olefins (MTO – methanol to olefins) or even selectively to propylene (MTP – methanol to propylene). These processes are indicated briefly in Fig. 4 with the acronym DH (dehydration processes) which comprises different types of processes, *e.g.* methanol to olefins, methanol to propylene and ethanol dehydration.

New routes under development are based on the direct Fischer–Tropsch (FT) reaction, *e.g.* direct use of syngas or even of CO₂–H₂ mixtures to selectively synthesize light olefins. To make sustainable the process, H₂ should be produced using RE sources (for example, by electrolysis using the electrical energy produced by hydropower or solar energy).

As indicated in Fig. 4, we have selected seven possible alternative routes to form olefins starting from biomass, biowaste and CO₂ (red arrows, indicated by a number such as ①). Scenario analysis refers to the European case. The first two routes are thermochemical, and consider the formation of gas (by gasification, or pyrolysis followed by gasification) and then conversion of syngas (for conciseness, we have omitted in Fig. 4 the need of a purification step, but this is one of the critical elements) either directly to olefins by FTO (Fischer–Tropsch to olefin) process (although catalysts for this reaction have to be further improved) or to methanol followed by MTO (methanol to olefin) or MTP (methanol to propylene) processes. The methanol synthesis is well established commercially, while MTO–MTP are industrial processes, even if there are still some critical aspects regarding productivity/deactivation.

The third route starts instead from CO₂ and renewable H₂, *e.g.* produced using RE and PEM electrolyzers (current preferable

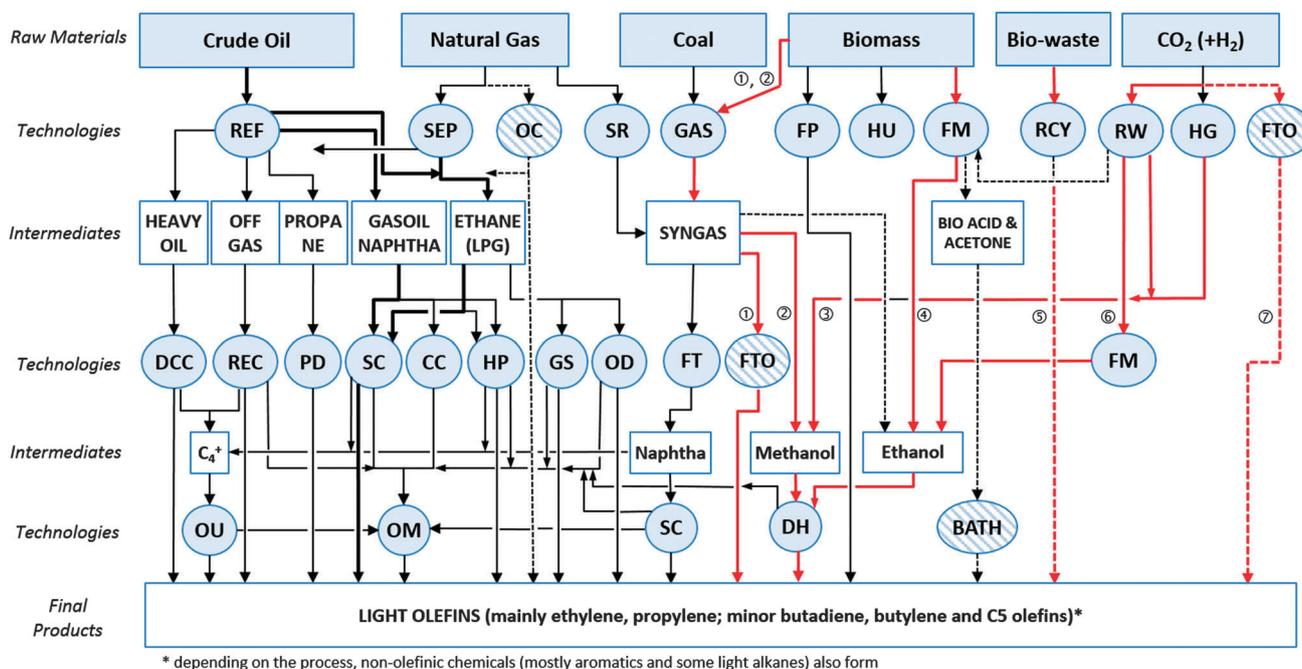


Fig. 4 Raw material and technology map in the production of light olefin. The paths in bold (black) are those mainly used today, while those in red indicate possible future routes starting from biomass, biowaste and CO₂, the latter with H₂ generated using renewable energy sources. Paths with a dashed line and technologies indicated with a background formed by parallel lines indicate paths/technologies still under development. The numbers in the red lines indicate the paths starting from biomass, biowaste and CO₂ that are discussed in the text. Re-elaboration from Fig. 3 of ref. 27. Acronyms: BATH: Bio-acid acetone to hydrocarbons (*e.g.* olefins); CC: Catalytic Cracking or Catalytic Pyrolysis; DCC: Deep Catalytic Cracking, etc.; DH: De-hydration process (*e.g.* methanol to olefins, methanol to propylene and ethanol dehydration); FM: Fermentation; FP: Flash pyrolysis; FT: Fischer–Tropsch synthesis; FTO: FT to olefin; GAS: Gasification and liquefaction; GS: Gas stream reactor technologies, *e.g.* shockwave reactors; HG: Hydrogenation; HP: Hydro-Pyrolysis; HU: Hydro-Thermal Upgrading Liquefaction which produces naphtha from biomass feedstock; OC: Oxidative coupling of methane; OD: Oxidative Dehydrogenation of ethane; OM: Olefin Metathesis, *e.g.* ABB-Lummus Olefin Conversion Technology, IFP-CPC meta-4; OU: Olefins Upgrading (conversion of C₄–C₁₀) to light olefins, *e.g.* Superflex, Propylur and Olefins Cracking; PD: Propane dehydrogenation; RCY: Re-cycling pyrolysis using organic waste such as discarded plastics, used rubber, etc.; REC: Recovery of refinery off gases, which contains ethylene, propylene, propane, etc.; REF: Refinery processes (distillation, catalytic cracking, cryogenic separation and absorption produces ethane and LPG, etc.); RW: reverse water gas shift; SC: Steam cracking (conventional); SEP: Gas separation process which produces methane, ethane and propane; SR: Steam Reforming of natural gas.

technology; high-temperature electrolysis has some advantages, but needs to be further developed). CO₂ may be directly hydrogenated to methanol, or instead CO₂ may be first converted to CO *via* reverse water gas shift reaction (RWGS). In the second case, the process is slightly more complex, but productivity is higher. Methanol can then be converted as above. This route depends considerably on the cost of production of renewable H₂, which in turn depends on the cost of electrical energy. We consider here the use of unused electrical energy sources (electrical energy which cannot be introduced to the grid, for example produced by wind during night, or in remote areas not connected to the grid). For CO₂, we consider the recovery from concentrated streams (for example, in some chemical and refinery processes or in biorefineries from fermentation) and that the reuse of CO₂ allows for a net introduction of RE in the process.^{11b}

The fourth path is based on the production of ethanol by fermentation, followed by dehydration to form ethylene. Production of other olefins would require to convert further ethylene, for example by olefin metathesis. This route depends greatly on the cost of production of ethanol. In Brazil, where cheap ethanol is available by sugar fermentation, already a couple of industrial plants (by Braskem, Dow and Solvay Indupa) produce ethylene from bioethanol, but the cost of ethanol production in Europe is greater. However, ethanol could be easily transported by ship, for example. Van Haveren *et al.*²⁹ indicated that bio-based ethylene production will significantly increase in the short and medium term, first in Brazil and then extending to regions such as USA and Europe. They suggested that this route would lead also to the production of bio-based vinyl chloride, with thus the two most dominant thermoplastic materials (polyethylene and polyvinylchloride) produced to a significant extent from biomass.

The fifth route considers the re-cycling pyrolysis using organic waste such as discarded plastics, used rubber, *etc.* The potential advantage is to avoid the costs of disposal of these wastes, but at the same time the use of waste does not guarantee a constant feed composition. There are also problems in terms of process and separation costs, as well purification. The sixth route is based on a first step of RWGS from CO-*ren.*H₂ mixtures, followed by a fermentation of the CO-H₂-CO₂ mixture to produce ethanol. LanzaTech has already developed some semi-commercial units for the second step of ethanol production, although productivity is still limited and ethanol has to be recovered from solution. Ethanol could then be dehydrated to ethylene as mentioned before. Renewable H₂ could derive also from processes using micro-organisms, such as cyanobacteria, able to produce H₂ using sunlight.

Finally, the last process considered is the direct conversion of CO₂-*ren.*H₂ mixtures by FT to the olefin process. This case assumes (as in route 1) that a yield of C₂-C₄ olefins >75% could be obtained. Although current data are still lower, this yield seems a reasonable target that can be reached.²⁸ These seven routes are compared with steam cracking of naphtha, the current most used process in Europe to produce light olefins. This route is considered as a reference for the olefin production by conversion of fossil fuel (conv. FF).

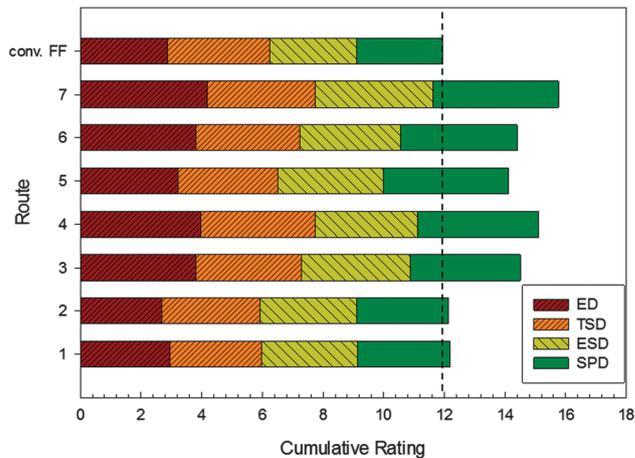


Fig. 5 Cumulative rating for the four drivers analysed to discuss the role of different routes (alternative to the use of fossil fuels) to produce olefins (from biomass, biowaste and CO₂) in relation to the future scenario for sustainable chemical production.

In order to evaluate the different routes, each of the drivers discussed before was sub-divided in various specific factors that were considered separately. These specific aspects are the following:

- ED: (i) cost of raw material *versus* product value; (ii) process complexity; (iii) investment necessary; (iv) integration with other processes.
- TSD: (i) technological barriers to develop the process; (ii) time to market; (iii) flexibility of the process; (iv) requirements for reaction and separation steps; (v) synergy with other process units.
- ESD: (i) energy efficiency; (ii) resource efficiency; (iii) environmental impact; (iv) GHG impact.
- SPD: (i) social acceptance; (ii) political drivers; (iii) public visibility.

A value between 1 (low) and 5 (high) was given to each of these specific factors, estimating then the value of ED, TSD, ESD and SPD by averaging the value of the relative specific aspects considered. The cumulative rating was the sum of the estimated value of each of these drivers (ED, TSD, *etc.*).

The results are reported in Fig. 5 that evidences how incentives (*e.g.* a higher cumulative rating) exist to use alternative raw materials to produce light olefins. It may be discussed the specific values assigned to each of the discussed drivers for the various routes analysed and in turn how this affects the relative ranking. However, this is not relevant. The result indicated from this discussion about the future scenario for the sustainable chemical production is that a multi-parameter analysis (rather than single aspects as typically used) indicates that there are motivations to develop novel sustainable olefin production routes.

2.2.2. Sustainable production of other olefins and polyolefins. Other olefins could be produced by alternative routes (to those based on fossil fuels as raw materials), but scenario analysis is less favourable than in the case discussed above. For example, various microorganism strains could produce propane and

propylene from glucose media (together with butane, butene, pentene, *etc.*), but productivity is low and separation costs high. Propylene could be produced from bio-chemical production of 1-propanol or 2-propanol *via* fermentation, but again actual productivity is still too low. Probably, the preferable route involves the production of 1,2-propanediol, converted to 2-propanol and finally dehydrated to propylene. The alternative is the ABE fermentation process leading to ethanol, butanol and acetone, the latter reduced to propylene. Also these routes, however, do not appear to be competitive. In fact, it would be preferable to use directly the glycols (1,2-propanediol, for example) obtained by catalytic conversion of sugars or other platform molecules (glycerol, lactic acid) as a substitute of those derived from fossil fuels. The latter are obtained by catalysed ring-opening of propylene oxide, for example. The glycol is then used to produce humectant, antifreeze or brake fluids and as a component of polyesters and alkyd resins. Polyol Chemical Inc., for example, is producing propylene and ethylene glycols (together with other products such as glycerine and butanediol) starting from sorbitol/glucose. The process economics, however, are positive only using waste sugar streams.

Butadiene is another interesting olefin that can be produced along different sustainable alternative routes (Fig. 6) with respect to the current process based on either the recovery from naphtha steam cracking fractions, or by dehydrogenation of butane. Butadiene could be produced by dehydrogenation of ethanol to acetaldehyde, followed by aldol condensation and dehydration. A one-pot process over MgO–SiO₂ catalysts (Lebedev process) is possible with an overall yield of 70% or more. Hüls has been using this process over three decades, but butadiene could only be economic using cheap bioethanol. Butadiene could be used to produce various rubbers, or converted (*via* epoxidation) to tetrahydrofuran and 1,4-butanediol.

Alternatively, 2,3-butanediol (2,3-BDO) produced by fermentation of sugars could be dehydrated to butadiene. LanzaTech has developed on a pilot-scale a fermentation process to produce 2,3-BDO (using CO–H₂ as feed). In a joint venture with other companies (Invista, a global nylon producer interested in converting butadiene to adiponitrile, an intermediate in the manufacture of Nylon 6,6) LanzaTech is also developing a process to convert 2,3-BDO to butadiene *via* fermentation (leading potentially to the single-step production of butadiene *via* gas fermentation). Versalis in a joint venture with Genomatica is also developing the production of butadiene *via* 2,3-BDO obtained by fermentation. There is a high potential

for these routes (by sugar or gas fermentation) to become commercially attractive, but still productivity and the cost of separation are critical elements.

Other olefins interesting for rubbers are also developed using biomass. Genecor in a joint venture with Goodyear is developing a bio-isoprene production process, and Glycos Biotechnologies plan also to commercialize the production of isoprene from crude glycerine. Global Bioenergies and Gevo/Lanxess are developing processes to produce isobutene from glucose or from isobutanol, respectively. The latter is produced by fermentation, as demonstrated on an already relatively large scale by Gevo and claimed to be competitive to the fossil-fuel based route to C₄ olefins.

However, butenes and butadiene can be produced from *n*-butane dehydrogenation or oxidative dehydrogenation. *n*-Butane cost, similar to other light alkanes in natural gas, has been decoupled from the oil price, due to the abundance of the market related to shale gas and the discovery of new gas fields. *n*-Butane can also be easily transported being a liquid under mild pressure. This fact, associated with the lower productivity in biobutanol or 2,3-BDO production by fermentation and lower selectivity as well (thus higher separation costs) with respect to bioethanol production by fermentation, make the bio-routes to C₄ olefins less attractive in comparison to the alternative path from *n*-butane. Notwithstanding the presence of various companies interested in developing bio-based intermediates for rubber manufacture, as discussed above, this scenario analysis thus indicates a less favourable outlook for producing biobutadiene with respect to the case of bioethylene. However, the use of cheap raw biomass and higher productivity micro-organisms could improve the process economics. As shown in Fig. 6, gas fermentation (from CO and in principle from CO₂) could be an alternative route based on waste streams (CO-rich emissions, for example).

2.2.3. Sustainable production of drop-in intermediates.

Various new routes are under development for the production of intermediates starting from biomass, biowaste or CO₂ as an alternative to current fossil-fuel based processes. An illustrative example is given from the production of 1,4-BDO. Current market is about 1.5 Mtons to produce polymers such as polybutylene terephthalate, copolyester ethers and thermoplastic polyurethanes. It can be converted to tetrahydrofuran (THF, used in some polymers synthesis or as a solvent) and to γ -butyrolactone (GBA), used in various syntheses for fine and speciality chemicals. Current production is a multi-step process, *via* synthesis of maleic anhydride (MA) by catalytic selective oxidation of *n*-butane, esterification of MA with ethanol followed by hydrogenation to diethylsuccinate converted then to GBA and finally to 1,4-BDO with THF as co-product. It is thus a complex multistep route, and thus a key advantage of alternative routes is the possibility to reduce the number of steps.

The current main alternative passes through the production of biosuccinic acid from sugars, eventually in the presence of CO₂. Various companies (BASF, DSM, Rochette, BioAmber, Purac, *etc.*) are working on pilot/demo scale production of biosuccinic acid. The latter can then be hydrogenated to BDO–THF. BDO can be alternatively produced by direct

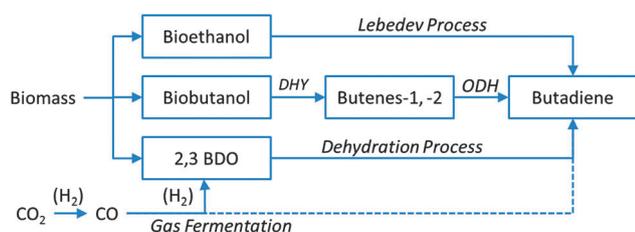


Fig. 6 Sustainable alternative routes to produce bio-butadiene. DHY: dehydration. ODH: oxidative dehydrogenation. 2,3-BDO: 2,3-butanediol.

fermentation of sugar (Genomatica), or *via* formation of PHA (polyhydroxyalkanoate) (Metabolix). The biosuccinic acid route is currently the most advanced, with a good potential to become a main route to produce BDO–THF, mainly because it reduces the process complexity and improves energy & resource efficiency with respect to the current path starting from *n*-butane.

Table 1 reports a list of processes to prepare drop-in intermediates for the chemical industry starting from biomass or biowastes. These processes are expected to be introduced commercially soon and become significant production routes. Table 1 also indicates the main companies involved in the development of these novel (sustainable) routes.³⁰

Table 2 reports instead already commercial or semi-commercial production routes of bio-based intermediates for the chemical industry.³⁰ The introduction of these routes (mainly focused at producing bioplastics) in the market shows impressive growth rates, as reported by European Bioplastics e.v. The worldwide production capacity for bioplastics will increase from around 1.2 million tonnes in 2011 to approxi-

mately 5.8 million tonnes by 2016, although still remaining a few percentage points of the global plastic market.

By far the strongest growth will be in the biobased, non-biodegradable bioplastics group, especially drop-in solutions, *i.e.* biobased versions of bulk plastics like PE (polyethylene) and PET (polyethylene terephthalate) deriving from fossil fuels. Leading the field is partially biobased PET, which is already accounting for approximately 40% of the global bioplastics production capacity. Partially biobased PET will continue to extend this lead to more than 4.6 million tonnes by 2016. That would correspond to 80% of the total bioplastics production capacity. Following PET is biobased PE with 250 000 tonnes, constituting more than 4% of the total production capacity. Biodegradable plastic market, particularly PLA (polylactic acid) and PHA (polyhydroxyalkanoates) each of them accounting for 298 000 tonnes (+60%) and 142 000 tonnes (+700%) respectively, also show rather high growth rates, but the market is much smaller in size. This analysis evidences that biobased, non-biodegradable commodity plastics (drop-in products such as PE, PET, or PP-polypropylene), are the main future route, being their possible use and recycling along their conventional counterparts.

2.2.4. Sustainable production of new intermediates and platform molecules. The previous section has emphasized the concept of drop-in products, *e.g.* which are produced by alternative raw materials without changing the final product already in commerce (however, quality may be different in terms of impurities). Biodegradable bioplastics will remain instead an interesting, but niche market, in part due to the fact that they are not drop-in products. Drop-in products can be faster commercialized, as it is not necessary to create a market and overcome the many barriers (authorization, REACH, *etc.*) necessary to introduce new chemicals/products.

There are, however, some relevant examples of non-drop-in chemicals which have a good potential to become large-scale products, because the final product has better properties and existing specific incentives (on the market) to products not derived from fossil fuels.

An example is offered by polyethylene furanoate (PEF) and its use as a new material for packaging. It must first be recalled that bottles and other packaging are the main areas of the use of bioplastic. These applications are thus expected to be the main areas for possible development of alternative bio-based chemicals to conventional ones. Between these, it can be cited especially the production of alternatives to PET, used mainly to produce bottles and food containers for the consumer markets. This market is sensitive to the green image of the product and thus there is interest from leading companies in this field (Coca Cola, Danone, for example) to use bio-based containers which reduce, if not eliminate, the use of fossil fuels.

A route of growing interest in this direction is that developed by Avantium for the synthesis of 2,5-FDCA (furan dicarboxylic acid) by oxidation of 5-HMF (5-hydroxymethyl-furfural), which can be obtained from fructose by dehydration.³¹ FDCA and MEG (mono ethylene-glycol) are then used to produce polyethylene furanoate (PEF), a valid alternative to PET with better

Table 1 Processes to prepare drop-in intermediates for the chemical industry starting from bio-mass/-waste³⁰

Product	Main companies involved in developing these routes
BTX	– Anellotech's Bio-BTX, Virent's BioFormPX – Paraxylene from Gevo's isobutanol
Adipic acid	– Verdezyne, Ronnovia, DSM, Genomatica, BioAmber
Acrylic acid	– OPX Biotechn./Dow Chem., Myriant, Novozyme/Cargill/BASF, ADM, Novomer, Metabolix
BDO	– Genomatica, Myriant, BioAmber, LanzaTech
Rubber feedstocks (butadiene, isoprene, isobutene)	– Butadiene – Amyris/Kuraray, LanzaTech/Invista, Versalis/Genomatica, Global Bioenergies/Synthos, Cobalt Biotechnologies – Isoprene – Amyris/Michelin, Ajinomoto/Bridgestone, DuPont/Goodyear, Aemetis, Glycos Biotechn. – Isobutylene – Global Bioenergies/LanzaTech, Gevo/Lanxess

BTX: benzene, toluene and xylenes. BDO: butanediol

Table 2 Commercial or semi-commercial production routes of bio-based intermediates for the chemical industry³⁰

Product	Process (company and starting raw material)
1,3-Propanediol	– Dupont from corn sugar – In China from glycerol
Butanol	– From corn by Cathay Industrial Biotech, Laihe Rockley and other small Chinese firms
Isobutanol	– Gevo from corn
Propylene glycol	– From glycerol by Oleon – From sorbitol by ADM
Ethylene glycol	– From corn glucose by Global Bio-Chem – From sugar-cane ethanol by Greencol and India Glycols
Epichlorohydrin	– From glycerol by Vinythai
Farnesene ^a	– From sugarcane by Amyris
Polyamides	– From castor-oil by many companies, such as Arkema, Evonik, BASF, Solvay, DSM, Radici Group, <i>etc.</i>

^a Farnesene refers to six closely related sesquiterpenes.

O₂-barrier capacity. MEG can also be produced from bio-resources, for example by one-pot catalytic conversion of cellulose in the presence of H₂.³² The reaction is quite selective and could be an alternative to the two-step current process involving the synthesis of ethylene oxide (EO) by ethylene epoxidation, followed by catalytic hydration of EO. It is thus possible to produce 100% biobased PEF which can substitute commercial PET (Fig. 6). The driving force for the development is from one side the social push to have more sustainable commodities and from the other the formation of a final product with superior performance (5-times higher resistance barrier to O₂ permeation).

Eerhart *et al.*³³ evaluated the energy and greenhouse gas (GHG) balance in the production of the bioplastic polyethylene furandicarboxylate (PEF) starting from corn based fructose and compared to its petrochemical counterpart polyethylene terephthalate (PET). The production of PEF can reduce the non-renewable energy use (NREU) approximately 40% to 50% while GHG emissions can be reduced approximately 45% to 55%, compared to PET for the system cradle to grave. These reductions are higher than for other biobased plastics, such as polylactic acid (PLA) or polyethylene (PE). With an annual market size of approximately 15 million metric tonnes (Mt) of PET bottles produced worldwide, the complete bottle substitution of PEF for PET would allow us to save between 440 and 520 PJ of NREU and to reduce GHG emissions by 20 to 35 Mt of CO₂ equivalents. If also substantial substitution takes place in the PET fibres and film industry, the savings increase accordingly. The GHG emissions could be further reduced by a switch to lignocellulosic feedstocks, such as straw, but this requires additional research.

The development of this route also opens the market to the use of the platform intermediate HMF (particular, when improved routes for the direct synthesis from cheaper raw materials such as cellulose can be developed) as well as of FDCA in a number of other applications.³¹ FDCA could be used to produce polyesters (for example, PEF for bottles, flexible packaging and carpets/textiles), co-polyesters (engineering resins), polyamides (for engineering plastics, nylons and fibers and bullet proof vests), polyurethanes (for footwear), thermosets (polyester resin for powder coating) and plasticizers (esters, for PVC cables).

HMF also finds use in other applications. Some of them are highlighted in Fig. 8 which reports some of the possible conversion routes to valuable high-volume chemicals. Between these routes, the following can be evidenced:

- *Caprolactam*: commercially produced in a multistep process from benzene; it is the monomer for Nylon-6.
- *1,6-Hexanediol*: commercially prepared by hydrogenation of adipic acid; it is widely used for industrial polyester and polyurethane production.
- *Adipic acid*: commercially produced in a multistep process from benzene; it is the monomer for Nylon-66.

Fig. 8 reports, as an example, the scheme of the catalytic synthesis of adipic acid from 2,5-FDCA, which can be made with an overall yield > 85%. Also the synthesis of the other two selected large-volume monomers could be realized with a high yield.

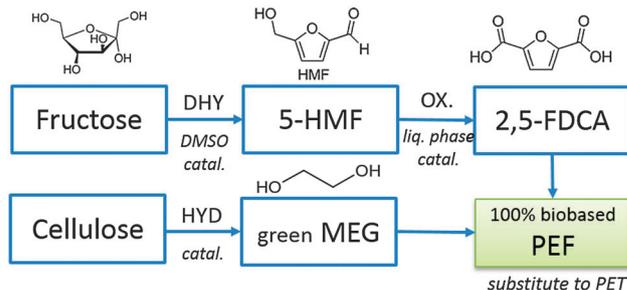


Fig. 7 Block-diagram for the production of 100% biobased PEF, as a substitute for oil-derived PET. DHY: dehydration. OX: selective catalytic oxidation.

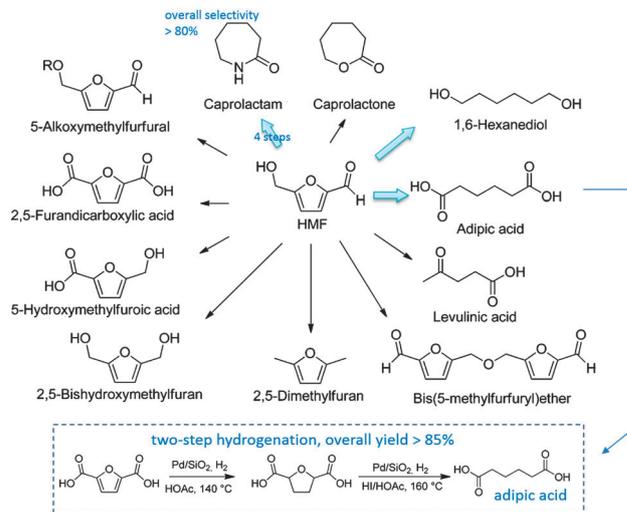


Fig. 8 HMF as platform molecule to produce chemicals and fuel components. The larger light-blue arrow indicates the three routes discussed in the text. In the bottom, the scheme of catalytic synthesis of adipic acid from 2,5-FDCA (one of the key products from HMF) is reported. Adapted from ref. 31, © ACS 2013.

Table 3 reports other interesting routes under development, in addition to those discussed above. Also these routes are potentially relevant for large-volume products and are based on alternative raw materials to fossil fuels (in part or full).

Table 3 Production routes under development based on alternative raw materials to fossil fuels (in part or full)³⁰

Product	Process under development
2,5-FDCA	- FDCA + MEG ⇒ PEF as alternative to PET - Nylons and Aramids using adipic acid derived from FDCA
CO/CO ₂	- CO ₂ + propylene oxide ⇒ polypropylene carbonate (PPC) - CO ₂ + ethylene oxide ⇒ polyethylene carbonate (PEC) - CO ₂ ⇒ polyether polycarbonate polyols (PPP) - CO + ethylene oxide ⇒ propiolactone - CO/CO ₂ ⇒ C2–C5 products (via FTO, GTL, or fermentation)
Levulinic acid (LA)	- LA ⇒ β-acetacrylic acid (new acrylate polymer) - LA ⇒ diphenolic acid (replacement for bisphenol-A) - LA ⇒ 1,4-pentanediol (new polyesters) - LA-derives lactones for solvent use

3. Role of catalysis in establishing the new scenario for the chemical industry

The previous section evidenced that there are many novel routes based on alternative raw materials (biomass, biowaste and CO₂) that are actively developed both at academic and industrial levels. As commented, these routes are at a different stage of development, and may have different chances to substitute current processes based on fossil fuel derived raw materials. A common aspect, however, is the need to improve process performances, typically by developing improved catalysts (a definition which includes bio-catalysis).

The discussion on the new scenario for the chemical industry has evidenced that some priority areas could be identified. This section will analyse the status and perspectives of catalysis in these areas, to identify the expected targets and possible breakthrough challenges, which in turn determines how fast and effective the transition to the new sustainable economy could be. Discussion is focused here on the use of solid catalysts, being in general their use preferable for more sustainable (resource and energy efficient) processes.

3.1 Catalysis for alternative routes of light olefin production

Light olefins are the building blocks for most of the petrochemistry routes and polymeric materials. The production of light olefins is thus one of the largest productions (mainly by steam cracking of naphtha in Europe), but is also very energy-intensive as commented before. The panorama for light olefin production is fast changing. There are two main challenges for their production (and thus for the petrochemical industry) in Europe. The first is the differing cost level of feedstocks and raw materials throughout the regions. The second is to cope with the age and the size of the existing plants in Europe. To maintain competitiveness, it is thus necessary to convert these challenges into new opportunities.

Regarding the cost of feedstocks, the last few years have seen a large capacity addition of petrochemical plants in the Middle East mainly based on associated gas from oil production leading to a superior cost position. In addition to that, the extensive shale gas exploration in the US leading to a substantial reduction of prices for natural gas and ethane was observed. As a result most cracker operators in the US have increased their share of lighter feedstocks and thus have experienced a significant improvement in their cost position. In Europe and Asia this change was not present, since availability of these NG feedstocks is and will probably remain limited.

But the advantage of lighter feedstocks comes at a price as these feedstocks result in a lower production of higher olefins. Propylene and crude C₄ are, meanwhile, an important factor for the competitiveness of naphtha crackers compared to ethane or light feed crackers. The existing supply shortage and the high demand for C₃ and C₄ are increasing their prices and thus the profitability of naphtha crackers.

Another important element regards the size of the plants for light olefin production. Steam-cracking plants have a typical size between 1.5 and 3.0 Mtons per year and they are not

profitable for smaller sizes or at lower operation capacity. It is thus necessary to transport the olefins at high distances, with associated costs and risks, and there is a low flexibility in operations. There is thus interest to develop dedicated, small size olefin production plants (on-purpose). Due to the shortage of propylene (mostly driven by increased consumption of PP, which is expected to expand by an average 5–6% for the next several years), new plants for propane dehydrogenation and olefin metathesis have been constructed, but the cost of propane (or *n*-butane for C₄ olefins–diolefins) is still high in Europe. Here there is the opportunity for the production of light olefins from alternative routes to fossil-fuel, because it can use (potentially) cheaper and more sustainable raw materials, and is suited for on-purpose production. Ethylene from bioethanol or CO₂ to olefins (FTO) are two of the interesting routes from this perspective.

3.1.1. Catalytic dehydration of ethanol. The simplified reaction mechanism of ethanol catalytic conversion over mixed oxides is presented in Fig. 9. Although this is a reaction apparently simple and acid-catalysed, it is necessary to tune the catalyst properties to maximize the selectivity, because it is necessary to avoid the (i) consecutive reaction of ethylene with surface acid sites, and (ii) redox reaction leading to dehydrogenation rather than dehydration. An acido-base concerted mechanism with formation of a surface ethoxy species occurs. This is an easy reaction occurring typically in very mild conditions and the rate limiting step of the reaction is thus water desorption to regenerate the active site.

γ -Alumina has been one of the first used catalysts for this reaction, but requires a high reaction temperature (450 °C) resulting in a relatively low ethylene yield (about 80%). Doping of the alumina with KOH and/or ZnO or the preparation of MgO–Al₂O₃/SiO₂ mixed oxides (Syndol catalyst) were used by companies such as Phillips Oil Co. and Halcon SD, respectively, to increase the selectivity. Further modifications with other dopants resulted in selectivities of over 98–99%, although high reaction temperatures were still necessary.

Zeolites, particularly H-ZSM-5, were a second class of catalysts used for ethanol dehydration. The main advantage is the activity at lower temperatures (200 to 300 °C). At 300 °C, HZSM-5 can reach an ethanol conversion level of 98% and 95% ethylene selectivity. The main disadvantage of HZSM-5 is its acidity, which reduces its stability and coking resistance. Modification with phosphorus to reduce acidity improves both

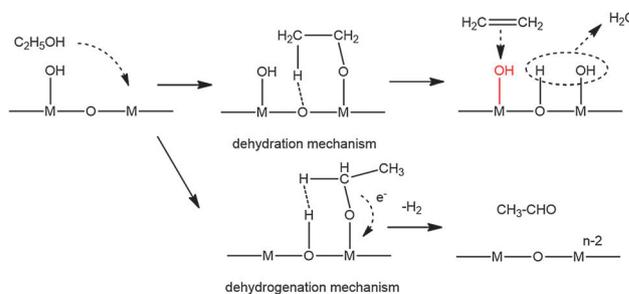


Fig. 9 Simplified reaction mechanism of ethanol conversion over mixed oxide catalysts.

selectivity (over 99%) and stability. Modification with La (eventually as co-dopant with P) leads also to interesting results. With almost 100% ethylene selectivity and ethanol conversion and low temperatures (about 240 °C), 0.5% La-2% P-HZSM-5 is currently one of the best catalysts for industrial use. Due to diffusional limitations, the use of nano-scale zeolites leads to better results. SAPO zeolites, such as SAPO-34 which is one of the best catalysts for methanol to olefin (MTO) reaction together with H-ZSM-5, also shows good performance in ethanol dehydration.

A third class of catalysts investigated was heteropolyacids. Particularly, $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ has demonstrated high catalytic ability, making it a promising catalyst for the dehydration of ethanol to ethylene, but its high acidity reduces its stability. This catalyst gives 99.2% selectivity at 100% ethanol conversion in rather mild conditions (220 °C, GHSV = 6000 h⁻¹),^{34a} but long term stability has to be demonstrated. As a comparison, an industrial catalyst such as the cited SynDol (Halcon) gives comparable performance (96.8% selectivity at 99% conversion), but requires higher temperatures (450 °C, LHSV = 26–234 h⁻¹).^{34b}

Therefore, recent developments in catalysts,^{34b,c} particularly nanoscale HZSM-5, which has a 99% ethylene yield at 240 °C and a lifespan of over 630 h before ethylene selectivity decreased to below 98%, and in heteropolyacids such as $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$, achieving over 99% ethylene yield at temperatures as low as 220 °C, have significantly improved performances over currently used catalysts in industrial plants for ethanol dehydration. We have to remark, however, that operations at low temperatures are not necessarily better (due to less efficient heat recovery), if not higher productivities and stability are achieved at the same time.

The profitability of the process depends essentially on the cost of production of bioethanol, which may vary considerably depending on the raw materials and technology of production. Energy integration of the process is also critical. Actual ethanol to ethylene plants have a production capacity about one order of magnitude lower than that typical of steam cracking plants, but this aspect could be an advantage in terms of on-purpose plants. Process intensification is one of the ways to make profitable also small-medium size plants.

3.1.2. CO₂ to olefins via FTO. There are different possible routes to produce light olefins from CO₂ and renewable H₂ (Fig. 10). RWGS reaction is typically promoted from the same

catalysts of the consecutive steps (methanol synthesis or FT reaction) and thus a single reactor/catalyst could be used. However, a direct route converting CO₂ without involving the RWGS step is preferable, because reversibility of the latter limits the performance. There are two main paths to light olefins: (a) a direct route from syngas (CO + H₂) using modified Fischer–Tropsch (FT) catalysts and (b) an indirect two-step route *via* the intermediate formation of methanol. In this indirect route, a conventional commercial methanol catalyst is used for the first step and small-pore zeolites (CHA or MFI-type) for the second methanol-to-olefin (MTO) step. In the presence of an acid catalyst, two methanol molecules could be dehydrated to dimethyl ether (DME), which can also be converted to light olefins (it is an intermediate in the process).

Being current methanol catalysts active both in RWGS reaction and in the methanol synthesis, it may be seem the same to start from CO–H₂ or CO₂–H₂ mixtures. However, the productivities in the second case are typically one third of those using syngas (CO–H₂), even if the addition of small amounts of CO₂ (less than 3–4%) to syngas promotes the methanol synthesis rate. There are two main motivations. CO₂ is a better oxidant than CO and thus in large amounts alters the surface active state of the catalysts (Cu–ZnO–Al₂O₃ based materials). The water formed in the RWGS reaction inhibits the reaction. It is thus convenient to use two reactors in series, with intermediate removal of water from the stream. The alternative is to use a reactor approach with *in situ* removal of water (catalytic distillation, membrane reactor). It is also possible to combine the catalysts for methanol to the zeolite for MTO to have in one-step the direct formation of light olefins from CO₂ and H₂.

In terms of R&D there are two main objectives. The first is to develop more productive catalysts for the direct use of CO₂–H₂ mixtures, which probably should be not active in the RWGS reversible reaction. It is necessary to remark that most of the catalysts tested up to now are based on catalysts for syngas (CO–H₂) adapted to operate with CO₂ and H₂, but not specifically developed to work with carbon dioxide. It would be desirable, for example, to have a novel FT catalyst able to directly and selectively convert CO₂ and H₂ to light olefins, or novel methanol catalysts able to directly convert CO₂ without the presence of the RWGS reaction. Therefore, even if the methanol, MTO and FT catalysts (from syngas) are well established and current methanol and FT processes operate in the presence of some carbon dioxide, converting pure CO₂ would require the development of novel or improved catalysts. Maximizing selectivity to light olefins, and possibly also their relative ratio of formation (currently it is preferable to form $\geq \text{C}_3$ over ethylene) is another challenge.

We focus here the discussion on the catalysts for the direct FTO conversion of CO₂ and *ren.*H₂ to light olefins, because this reaction would be preferable for a resource and energy efficient process.

The probability for the selective formation of lower olefins increases with temperature (in the 200–400 °C temperature range, the typical one for FT reaction) and decreases at higher pressures and H₂:CO ratios in the feed. Olefins can also be incorporated into the growing chain involving a metallocyclobutane transition state followed by β -H transfer to

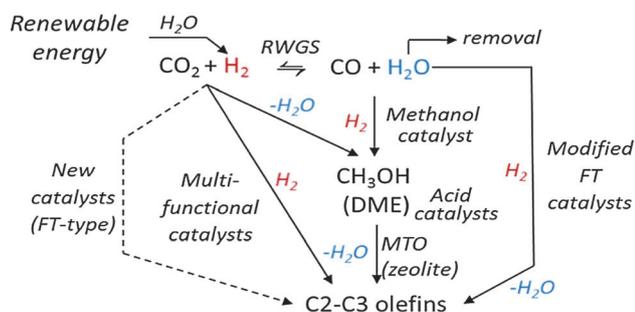


Fig. 10 Different routes to synthesize light olefins from CO₂ and renewable H₂. Reproduced with permission from ref. 11b. © RCS 2013.

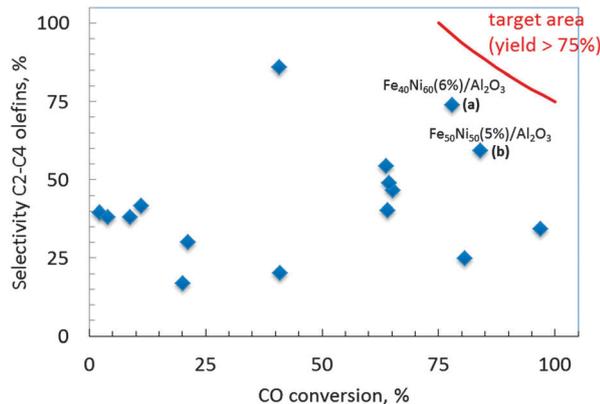


Fig. 11 Relevant literature results in FTO reaction (see ref. 11b and 28 for references) starting from syngas, with an indication of the target yields for possible industrial exploitation. Composition of two of the better catalysts formulations is also indicated (data refer to a temperature of 360 °C): (a) ref. 35a. (b) ref. 35b.

form a α -olefin. It is thus necessary to prevent the re-adsorption of olefins which increases the formation of longer-chain compounds. Shorter contact times are preferable, but also the choice of the reactor is important. Operations in liquid phase (slurry-type reactors) allow limiting olefin readsorption and surface overheating due to the exothermic reaction. Operations in a slurry reactor lead to maximizing the yields of lower olefins.

Fig. 11 reports selected relevant literature results^{11b,28} in the FTO reaction starting from syngas, because up to now the studies using $\text{CO}_2\text{-H}_2$ instead of CO-H_2 (eventually with small amounts of CO_2) are limited. Fig. 10 also indicates the target area from an industrial perspective. In general, overall, yields up to over 55% in C2–C4 olefins have been observed, but together with C2–C4 alkanes, methane and C5+ products.³¹ These conditions are still not satisfactory and a further improvement would be necessary, to start from CO_2 instead of that from CO. There is thus the need for further R&D on catalysis to develop and exploit this route.

3.1.3. Catalytic synthesis of butadiene. Butadiene is predominantly sourced by extraction from the mixed C4 stream produced in steam crackers, particularly of naphtha sources. Historically the revenue from these valuable co-products maintained margins for cracking naphtha at a premium to cracking lighter natural gas liquids. This situation, however, is changing quickly, and there is thus interest in bio-routes to produce butadiene, particularly for on-purpose applications. The catalytic dehydrogenation or oxidative dehydrogenation of *n*-butane, however, is a strong competitive route.

There are some main possibilities to produce butadiene by alternative, non-fossil-fuel based routes (Fig. 6). The process to convert ethanol into butadiene is not new, but still rather inefficient. Ethanol is converted into acetaldehyde after which an aldolization is performed followed by dehydration. A target yield of over 90%, at temperatures below about 450 °C, is required for industrial exploitability, and good stability as well. A selection of catalytic results³⁶ is reported in Fig. 12.

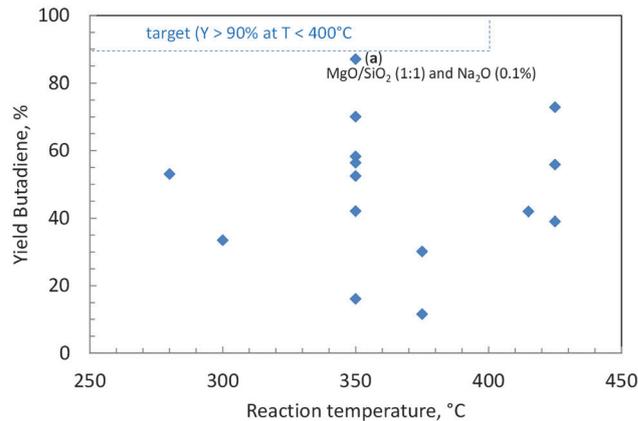


Fig. 12 Catalytic synthesis of butadiene from bioethanol. Composition of the better catalyst is also indicated. (a) ref. 37. Based on the data reported in Table 7 of ref. 36. © Wiley 2013.

While in general yields were unsatisfactory (below 70%), a catalyst based on magnesia-silica, doped with Na_2O , has been reported having performances close to the target.³⁷ However, the results have not been reproduced later by other authors. There is thus the need to develop improved catalysts for this reaction, as well as to understand a number of fundamental aspects (reaction mechanism, structure–activity–selectivity relationship, *etc.*).³⁶

In the evaluation (using a multi-criteria approach) of different routes for using bioethanol as a chemical building block for biorefineries, Posada *et al.*³⁸ indicates the conversion of ethanol to ethylene or 1,3-butadiene as promising routes for an integrated biorefinery concept, in contrast to other possibilities (for example, ethanol conversion to acetic acid, *n*-butanol, isobutylene, hydrogen and acetone).

Butanol dehydration to butenes and butadiene has been presented as a valuable route,³⁹ but we would instead suggest that it is necessary to produce the raw material at a more competitive cost. In addition, the further catalytic conversion to butadiene is also difficult. While ethanol to ethylene conversion is a dehydration reaction, butanol conversion to butadiene requires an oxidative dehydration–dehydrogenation mechanism. Data are quite limited on this reaction and related catalysts.

The third alternative is the conversion of butanediol to butadiene, which is investigated by companies such as LanzaTech and Genomatica/Versalis. 1,3-, 1,4- or 2,3-butanediol could be dehydrated to butadiene over acid catalysts, but various byproducts (unsaturated alcohol, ketone, *etc.*) form and the reaction is thus more challenging with respect to ethanol dehydration.

ABE fermentation (acetone–butanol–ethanol) with wild and genetically modified strains (from the *Clostridium* family) has been known for a long time, but has received renewed interest recently. However, there are still many aspects to improve in order to produce *n*-butanol at commercially attractive prices, such as (i) improve yields of butanol, (ii) expanding substrate utilization and (iii) minimizing energy consumption during separation and purification. The cost of *n*-butanol is thus still high. It is necessary to develop micro-organisms able to give the selective fermentation to butanol to make competitive the synthesis.

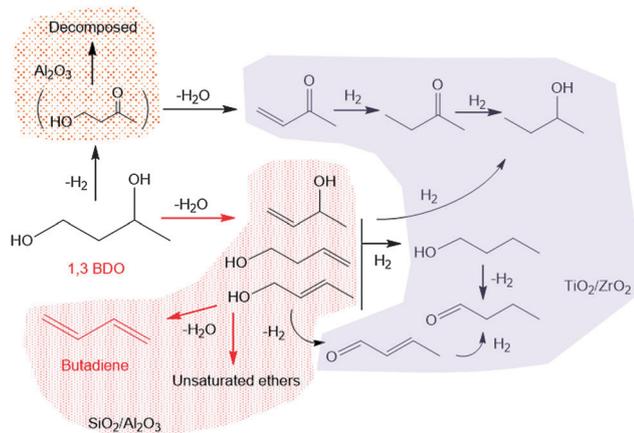


Fig. 13 Reaction network in the conversion of 1,3-BDO to butadiene and other products on mixed oxides. The coloured areas indicate the prevailing mechanism of transformation over the oxides indicated in the coloured area. Adapted from ref. 40. © Elsevier 2006.

Solid acids such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, Al_2O_3 , ZrO_2 and TiO_2 convert 1,3-butanediol (1,3-BDO) depending on their acid properties (Fig. 13).⁴⁰ Strong acid catalysts ($\text{SiO}_2\text{-Al}_2\text{O}_3$) catalyse the dehydration of 1,3-butanediol at reaction temperatures below 250 °C, while weak acid catalysts (ZrO_2 and TiO_2) require temperatures above 325 °C. $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyses the dehydration of 1,3-butanediol into unsaturated alcohols. The latter are then dehydrated into 1,3-butadiene. Alumina alone instead forms 4-methyl-1,3-dioxane, which is the acetal compound of 1,3-butanediol and formaldehyde. Several compounds were produced over TiO_2 and ZrO_2 owing to the side reactions such as dehydrogenation and hydrogenation. On strong solid acids, the butadiene selectivity is still unsatisfactory and thus more research is needed.

On the other hand, the method could be interesting for the synthesis of unsaturated alcohols (raw materials for the synthesis of various fine and speciality chemicals for applications such as medicines, perfumes, agricultural products). Over weak basic oxides such as CeO_2 at 325 °C, 3-buten-2-ol and *trans*-2-buten-1-ol are produced with selectivities of about 58% and 36%, respectively.⁴¹

3.2 Catalysis for platform molecules

Section 2.2.4 evidenced how HMF and its derivatives (Fig. 7 and 8) are good platform molecules³¹ to produce important chemicals according to alternative routes to commercial production starting from fossil fuels.

3.2.1. Catalytic synthesis of 5-hydroxymethylfurfural (HMF).

Among the platform chemicals which can be obtained from biomass (for example, levulinic acid or bioethanol), HMF shows some distinctive advantages: (i) it has retained all six carbon atoms present in the hexoses and (ii) high selectivities are possible in its preparation, in particular from fructose. Current (year 2013) cost for fructose syrup is about 0.6 \$ kg^{-1} , making it possible to produce HMF at a cost of around 0.9–1.0 \$ kg^{-1} , which is suitable for the chemicals discussed below, but not for fuels, except some booster additives.

HMF forms by acid-catalysed dehydration of hexoses. Fructose is much more reactive and selective toward HMF than glucose,

because the latter has a more stable ring structure, which hinders its ability to form the cyclic reaction intermediate. It is thus necessary to isomerize glucose to fructose, if starting from the former. The solvent influences the tautomeric forms present in solution and thus reactivity (even if there is a fast interconversion between them). Therefore, the solvent plays a key role in both reactivity and selectivity.

Fructose dehydration to HMF has been known for a long time, but only relatively recently have high HMF yields been obtained working in organic solvents. Both homogeneous and heterogeneous acid catalysts could be used, but the latter are preferable for an industrial process. Fig. 14 summarizes selected catalytic results (using solid catalysts) obtained in aqueous systems or in organic solvents.³¹ Target yield ($\geq 95\%$) is also indicated. As shown from the figure there are some catalysts meeting the requirements. The table in Fig. 14 shows some of the catalyst compositions and relative operating conditions, which meet the target HMF yield. Relatively mild reaction conditions are necessary (about 120 °C, 2 h of reaction), but it is important that good yields are obtained also with high fructose concentrations. Dimethyl sulfoxide (DMSO) is the best solvent, but also acetone–DMSO mixtures as well as dimethylformamide (DMF) give good results. Very high yields ($>90\%$) are found for a number of catalysts, such as zeolites, heteropolyacids and acidic resins in DMSO, but in general a continuous water removal is necessary. Amberlyst 15 is claimed to yield 100% HMF, even after recycling (three times) and at fructose concentrations as high as 50%.⁴² In the case of $\text{FePW}_{12}\text{O}_{40}$ and H-BEA zeolite, the HMF yields decreased to below 50% at 50 wt% fructose concentration, while yields $>90\%$ at low fructose concentration.

The same catalysts giving excellent yield in HMF from fructose show lower performances starting from glucose, and

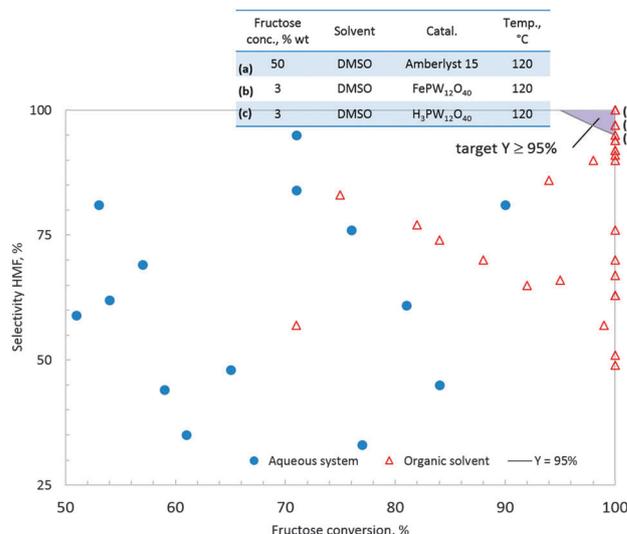


Fig. 14 Catalytic synthesis of HMF from fructose in aqueous systems or organic solvent. Composition of the better catalyst is also indicated. (a–c) ref. 42. Based on the data reported in Tables 9 and 12 of ref. 31. © ACS 2013.

even worse starting from polysaccharides. The HMF yields from cellulose are generally very low (<10%). There is thus the need to develop novel multifunctional catalysts for the selective HMF synthesis starting from polysaccharides. Taking into account the price differential with respect to fructose, a target yield over 60% has to be obtained.

The use of ionic liquids (IL) to overcome the limits of solubility in water–organic solvents of some polysaccharides, and to improve performances starting from the latter is an active research line.³¹ However, to apply IL as reaction media for HMF production from biomass, highly efficient recycling is required because of their high cost. Another challenge is related to progressive contamination of IL when using untreated biomass feedstock, because these contain many inorganic (ash) and organic impurities that should be periodically removed from the IL.

3.2.2. Catalytic conversion of HMF. As discussed before, HMF could be converted to a variety of valuable chemicals/intermediates, but the synthesis of 2,5-FDCA, caprolactam, caprolactone and 1,6-hexanediol are more interesting.

HMF oxidation into FDCA was achieved in the past using different stoichiometric oxidants like N_2O_4 , HNO_3 and KMnO_4 , but today a cleaner catalytic synthesis is necessary. The oxidation of HMF using air or O_2 could be achieved by different catalysts. Catalysts such as those currently used for terephthalic acid production (Co/Mn/Br) could be used at high pressure (70 bar air), but operations using heterogeneous catalysts would be preferable. Between the most active/selective catalysts reported recently, it may be cited.

– Pt supported on carbon or Al_2O_3 gives 98% FDCA yield at complete HMF conversion in the liquid phase oxidation with oxygen in the presence of a base (need to keep the FDCA formed in aqueous solution as dialkalinic salt);^{42a} reaction conditions are 100 °C, 40 and 260 min for C and alumina supports respectively, and 150 psi O_2 .

– Au supported on hydrotalcite, which under similar reaction conditions as above, gives nearly 100% FDCA yield.^{42b} This catalyst, due to the use of a basic support, may avoid the use of a base, the base being the support itself. However, strong chemisorption of FDCA on the support may cause incomplete recovery and possible catalyst deactivation over time. In addition, Pt-based catalysts oxidize HMF to FDCA an order of magnitude faster than Au-based catalysts.

The use of bimetallic catalysts, for example Au–Cu/ TiO_2 giving 99% FDCA yield at 110 °C for 4 h under 20 bar O_2 ,⁴³ improves catalyst stability, but remains a critical aspect in these catalysts.

Direct synthesis routes of FDCA from fructose by combining dehydration and oxidation have also been reported using Pt–Bi/C in combination with a solid acid in water–MIBK. However, an FDCA yield of only 25% was obtained. Direct (base-free) oxidative esterification of HMF into the diester (which may be directly used to produce polymers) was instead demonstrated by Casanova *et al.*⁴⁴ using Au/ CeO_2 as catalyst in methanol under 10 bar oxygen in an autoclave reactor (yield about 99% at about 65 °C).

Therefore, although some improvements in catalysts could still be necessary, for example to avoid the use of a base and to have more stable operations, catalysts for the selective oxidation of HMF to FDCA are available.

As outlined in Fig. 8, several other compounds can be made from HMF, eventually *via* intermediate FDCA formation. Adipic acid, used in the synthesis of nylon 6,6, synthesis from HMF is one of the most attractive routes. The hydrogenation of FDCA to adipic acid occurs in a two-step process.⁴⁵ In the first step, 2,5-tetrahydrofuran-dicarboxylic acid is produced in 88% yield by hydrogenating FDCA at 140 °C for 3 h in acetic acid, catalyzed by Pd on silica. Yields up to 99% of adipic acid were claimed by reacting this product under hydrogen at 160 °C for 3 h in acetic acid in the presence of 0.2 M of HI and 5% Pd on silica catalyst.

A multistep route to produce caprolactam (the monomer for nylon-6) or 1,6-hexanediol (monomer for high performance polyesters, polyurethane resins, and adhesives) has been proposed by de Vries and co-workers (Fig. 14).⁴⁶ HMF is hydrogenated in >99% yield to 2,5-bishydroxymethyl-tetrahydrofuran which can then be further hydrogenated to 1,6-hexanediol in 86% yield, by using a Rh–Re/ SiO_2 catalyst in the presence of Nafion. This is a tandem three step process proceeding through formation of 1,2,6-hexanetriol, which is cyclized under the influence of the acid to tetrahydropyran-2-methanol, which in turn is hydrogenated to 1,6-hexanediol using the same catalyst. The diol can then be converted into caprolactone using a ruthenium catalyzed Oppenauer oxidation in virtually quantitative yield. Overall selectivity from HMF to caprolactone was 86%. Conversion of ϵ -caprolactone into caprolactam can be made selectively using ammonia at 170 bar and 300–400 °C (UCC process), but an alternative catalytic route would be preferable (Fig. 15).

HMF could thus be converted to caprolactam in a 4 steps process, whereas the current industrial process, which is based on benzene, contains seven steps. Using this technology, producing 1 kg of caprolactam would require 1.44 kg of HMF, 0.11 kg of H_2 , and 0.17 kg of NH_3 . These results indicate the interest in this novel process using renewable resources, but it is necessary to improve the productivity of the steps, particularly of the diol to caprolactone step for which the development

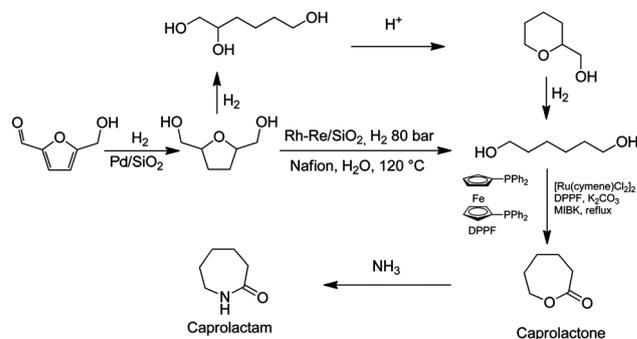


Fig. 15 Catalytic conversion of HMF into caprolactam or 1,6-hexanediol. Adapted from Scheme 42 of ref. 31. © ACS 2013.

of heterogeneous catalysts appears necessary. Combining this step with the consecutive one, *e.g.* developing direct catalysts for 1,6-hexanediol to caprolactam, would be also useful.

There are thus various attractive routes by which important monomers can be synthesized in alternative routes to those currently based on fossil fuels. For conciseness, we have limited the discussion here to the use of HMF as a renewable platform molecule, but there are other important possibilities. One of these is glycerol, produced in large amounts as a by-product during bio-diesel production.⁴⁷

Glycerol can be catalytically converted to C3 diols (alternative method to the production by fermentation, or from propylene). 1,2-Propanediol (1,2-PDO or propylene glycol; it is currently produced from propylene *via* propene oxide) is used as a chemical feedstock for the production of unsaturated polyester resins. Other relevant uses are as humectant (E1520), solvent, and preservative in food and for tobacco products, including in electronic cigarettes. 1,3-Propanediol (1,3-PDO) has a wide range of applications from carpets and textiles to cosmetics, personal, and home care industry. Polytrimethylene terephthalate (PTT, mainly used in the carpet industry) is the largest application of 1,3-PDO. It also has the potential to substitute propylene glycol, 1,4-butanediol (BDO), butylenes glycol, and nylon in a number of applications. Glycerol can be also dehydrated to acrolein and then oxidized to acrylic acid and acrylate esters,⁴⁸ which are also important monomers for polymer industry. The main current limitation to industrial development of these processes is the large uncertainty in defining the long-term trend in the price of glycerol. This is one of the main motivations having inhibited the industrial exploitation of these processes.

Acrylic acid can be also produced from CO₂ and ethylene.⁴⁹ Although important progress has been made recently in particular by BASF researchers, to realize this reaction on an industrial scale, it is still a challenge. Using ethylene from bioethanol, a full alternative renewable route to acrylic acid and derivatives could be realized.

4. Conclusions

The use of biomass, bio-waste and CO₂ derived raw materials, the latter synthesized using H₂ produced using renewable (solar) energy sources, open up new scenarios to developing a sustainable and low carbon chemical production, particularly in regions such as Europe lacking in other resources. There are many motivations for this transition to a new economy and some of them are also discussed in the Introduction. Typically in the transition to new economies, there is the start of many R&D initiatives to explore new possibilities and new synthetic routes, even though only a minimal part of them will be effectively exploited as main synthetic routes.

It is thus necessary to have some guidelines to analyse these alternative routes, and determine those having better possibilities to become future main routes of production. This tutorial review discusses first this new scenario, in particular from a sustainability perspective, with the aim to point out, between

the different possible options, those more relevant to enable this new future scenario for chemical production. In particular the different drivers (economic, technological and strategic, environmental and sustainability and socio-political) guiding the selection are commented upon.

The case of the use of non-fossil fuel based raw materials for the sustainable production of light olefins is discussed in a little more detail, but the production of other olefins and polyolefins, of drop-in intermediates and other platform molecules are also analysed. These examples will not systematically cover the entire possibilities, it not being possible given the limits of a tutorial review, but are valuable cases of the aspects to consider.

The final part discusses the role of catalysis in establishing this new scenario, summarizing the development of catalysts with respect to industrial targets, for (i) the production of light olefins by catalytic dehydration of ethanol and by CO₂ conversion *via* FTO process, (ii) the catalytic synthesis of butadiene from ethanol, butanol and butanediols, and (iii) the catalytic synthesis of HMF and its conversion to 2,5-FDCA, adipic acid, caprolactam and 1,6-hexanediol. Also in this case, other valuable platform molecules are possible (the case of glycerol is briefly discussed).

We have also limited the discussion about CO₂ conversion routes (except for the case of CO₂ to FTO), because these have been discussed in detail elsewhere.^{1,11b,12} To mention, however, that the conversion of CO₂ over novel designed electrocatalysts for photoelectro-catalytic (artificial-leaf like) devices⁵⁰ opens new perspectives to move to what is defined as Economy 3.0, *e.g.* where a distributed energy and chemical production will exist.

In conclusion, the panorama for chemical production is fast evolving and new raw materials, substituting fossil fuels for sustainability motivations and to develop a low carbon society, will become a main driver to develop novel production routes. Catalysis is a key element to enable this possibility. Starting from scenario analysis to selecting the key routes, we have examined the status of development and some of the remaining critical aspects on which to focus the research.

Acknowledgements

The authors acknowledge the PRIN10-11 projects “Mechanisms of activation of CO₂ for the design of new materials for energy and resource efficiency” and “Innovative processes for the conversion of algal biomass for the production of jet fuel and green diesel” for the financial support.

References

- 1 G. Centi and S. Perathoner, *ChemSusChem*, 2014, DOI: cssc.201300926.
- 2 (a) F. Cavani, G. Centi, S. Perathoner and F. Trifirò, *Sustainable Industrial Chemistry: Principles, Tools and Industrial Examples*, Wiley-VCH, Germany, 2009; (b) G. Centi and R. A. van Santen, *Catalysis for Renewables*, Wiley-VCH, Germany, 2007.

- 3 (a) J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164; (b) D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem. Soc. Rev.*, 2012, **41**, 8075.
- 4 H. Kobayashi and A. Fukuoka, *Green Chem.*, 2013, **15**, 1740.
- 5 (a) G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044; (b) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411.
- 6 S. Zinoviev, F. Müller-Langer, P. Das, N. Bertero, P. Fornasiero, M. Kaltschmitt, G. Centi and S. Miertus, *ChemSusChem*, 2010, **3**, 1106.
- 7 M. Stocker, *Angew. Chem., Int. Ed.*, 2008, **47**, 9200.
- 8 R. Rinaldi and F. Schüth, *Energy Environ. Sci.*, 2009, **2**, 610.
- 9 P. Gallezot, *ChemSusChem*, 2008, **1**, 734.
- 10 A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621.
- 11 (a) G. Centi and S. Perathoner, *Catal. Today*, 2009, **148**, 191; (b) G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711.
- 12 E. A. Quadrelli, G. Centi, J.-L. Duplan and S. Perathoner, *ChemSusChem*, 2011, **4**, 1194.
- 13 M. Aresta and A. Dibenedetto, *Dalton Trans.*, 2007, 2975.
- 14 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.
- 15 W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703.
- 16 M. Peters, B. Kohler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Muller, *ChemSusChem*, 2011, **4**, 1216.
- 17 K. Triantafyllidis, A. Lappas and M. Stöcker, *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, Elsevier, The Netherlands, 2013.
- 18 M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Germany 2010.
- 19 J. Mao, K. Li and T. Peng, *Catal. Sci. Technol.*, 2013, **3**, 248.
- 20 S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem., Int. Ed.*, 2013, **52**, 7372.
- 21 S. Navalon, A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *ChemSusChem*, 2013, **6**, 562.
- 22 W. Fan, Q. Zhang and Y. Wang, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2632.
- 23 V. P. Indrakanti, J. D. Kubicki and H. H. Schobert, *Energy Environ. Sci.*, 2009, **2**, 745.
- 24 W. Bello, *De-Globalization: Ideas for a New World Economy*, Zed Books, London, UK, 2005.
- 25 (a) G. Centi, P. Lanzafame and S. Perathoner, *Catal. Today*, 2011, **167**, 14; (b) G. Centi, P. Lanzafame and S. Perathoner, *Catal. Today*, 2013, submitted.
- 26 F. Cavani and J. H. Teles, *ChemSusChem*, 2009, **2**, 508.
- 27 T. Ren, M. Patel and K. Blok, *Energy*, 2006, **31**, 425.
- 28 G. Centi, G. Iaquaniello and S. Perathoner, *ChemSusChem*, 2011, **4**, 1265.
- 29 J. van Haveren, E. L. Scott and J. Sanders, *Biofuels, Bioprod. Biorefin.*, 2008, **2**, 41.
- 30 D. de Guzman, Bio-Based Chemical Feedstocks, presented at Tecnon OrbiChem Marketing Seminar at APIC 2013, Taipei, 9 May 2013.
- 31 R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499.
- 32 A. Wang and T. Zhang, *Acc. Chem. Res.*, 2013, **46**, 1377.
- 33 A. J. J. E. Eerhart, A. P. C. Faaij and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 6407.
- 34 (a) J. Gurgul, M. Zimowska, D. Mucha, R. P. Socha and L. Matachowski, *J. Mol. Catal. A: Chem.*, 2011, **351**, 1; (b) D. Fan, D.-J. Dai and H.-S. Wu, *Materials*, 2013, **6**, 101; (c) M. Zhang and Y. Yu, *Ind. Eng. Chem. Res.*, 2013, **52**, 9505.
- 35 (a) M. Feyzi, A. A. Mirzaei and H. R. Bozorgzadeh, *J. Nat. Gas Chem.*, 2010, **19**, 341; (b) C. Wang, L. Xu and Q. Wang, *J. Nat. Gas Chem.*, 2003, **12**, 10.
- 36 C. Angelici, B. M. Weckhuysen and P. C. A. Bruijninx, *ChemSusChem*, 2013, **6**, 1595.
- 37 R. Ohnishi, T. Akimoto and K. Tanabe, *J. Chem. Soc., Chem. Commun.*, 1985, 1613.
- 38 J. A. Posada, A. D. Patel, A. Roes, K. Blok, A. P. C. Faaij and M. K. Patel, *Bioresour. Technol.*, 2013, **135**, 490.
- 39 M. Mascal, *Biofuels, Bioprod. Biorefin.*, 2012, **6**, 483.
- 40 N. Ichikawa, S. Sato, R. Takahashi and T. Sodesawa, *J. Mol. Catal. A: Chem.*, 2006, **256**, 106.
- 41 S. Sato, F. Sato, H. Gotoh and Y. Yamada, *ACS Catal.*, 2013, **3**, 721.
- 42 (a) M. A. Lilga, R. T. Hallen and M. Gray, *Top. Catal.*, 2010, **53**, 1264; (b) N. K. Gupta, S. Nishimura, A. Takagaki and K. Ebitani, *Green Chem.*, 2011, **13**, 824; (c) K.-I. Shimizu, R. Uozumi and A. Satsuma, *Catal. Commun.*, 2009, **10**, 1849.
- 43 T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J. A. Lopez-Sanchez, M. Sankar, Q. He, C. J. Kiely, G. J. Hutchings and F. Cavani, *Green Chem.*, 2011, **13**, 2091.
- 44 O. Casanova, S. Iborra and A. Corma, *J. Catal.*, 2009, **265**, 109.
- 45 T. R. Boussie, E. L. Dias, Z. M. Fresco and V. J. Murphy, *Int. Patent WO*, 2010144873, 2010, (assigned to Rennovia, Inc.).
- 46 T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries and H. J. Heeres, *Angew. Chem., Int. Ed.*, 2011, **50**, 7083.
- 47 C. H. Zhou, H. Zhao, D. S. Tong, L. M. Wu and W. H. Yu, *Catal. Rev. Sci. Eng.*, 2013, **55**, 369.
- 48 B. Katryniok, S. Paul and F. Dumeignil, *ACS Catal.*, 2013, **3**, 1819.
- 49 M. L. Lejkowski, R. Lindner, T. Kageyama, G. E. Bodizs, P. N. Plessow, I. B. Müller, A. Schaefer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk and M. Limbach, *Chem.-Eur. J.*, 2012, **18**, 14017.
- 50 (a) S. Bensaid, G. Centi, E. Garrone, S. Perathoner and G. Saracco, *ChemSusChem*, 2012, **5**, 500; (b) C. Genovese, C. Ampelli, S. Perathoner and G. Centi, *J. Energy Chem.*, 2013, **22**, 202; (c) C. Ampelli, R. Passalacqua, C. Genovese, S. Perathoner and G. Centi, *Chem. Eng. Trans.*, 2011, **25**, 683; (d) C. Ampelli, R. Passalacqua, S. Perathoner and G. Centi, *Chem. Eng. Trans.*, 2009, **17**, 1011.