

# Realizing Resource and Energy Efficiency in Chemical Industry by Using CO<sub>2</sub>

G. Centi, S. Perathoner and G. Iaquaniello

**Abstract** A competitive and sustainable chemical industry requires developing new strategies for resource and energy efficiency. We present here the concept that the use of CO<sub>2</sub> offers innovative possibilities to achieve this objective. The routes, opportunities, and barriers in converting CO<sub>2</sub> using renewable energy and their impact on the chemical and energy value chains are discussed after introducing the general aspects of this topic evidencing the tight integration between the CO<sub>2</sub> use and renewable energy insertion in the value chain of process industry. The specific challenge of using CO<sub>2</sub> for the production of light olefins (ethylene, propylene), as specific example of value of carbon dioxide as carbon source to meet both resource and energy efficiency, is discussed. The conversion of CO<sub>2</sub> back to fuels using sunlight (solar fuels) is also discussed to evidence how is a relevant opportunity to develop effective energy vectors for the storage of solar energy which integrates into existing energy infrastructure and allow a smooth, but fast transition to a more sustainable energy in future.

**Keywords** CO<sub>2</sub> use · Renewable energy · Solar fuels · Olefin from CO<sub>2</sub> · Resource efficiency

## 1 Introduction

Realizing a sustainable, resource-efficient, and low-carbon economy is a major current challenge for society [1]. It is undoubtedly the role of the chemical industry to achieve this goal. Even if large progresses in this direction have been made over

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G. Centi (✉) · S. Perathoner  
Dipartimento di Ingegneria Elettronica, Chimica ed Ingegneria Industriale,  
University of Messina and INSTM/CASPE, V.le F. Stagno D'Alcontres 31,  
98166 Messina, Italy  
e-mail: centi@unime.it

G. Iaquaniello  
KT-Kinetics Technology, V.le Castello della Magliana 75, 00148 Rome, Italy

the last two decades, a systemic change in the way energy and raw materials are used is necessary in a world of finite resources and with a rapidly growing population. The novel aspect is that chemical industry is realizing now that this approach could be a winning opportunity for increasing competitiveness and innovation in the chemical industry. In Europe, most of the activities are centered on the initiatives around the European Technology Platform of Sustainable Chemistry (ETP SusChem, [www.suschem.org](http://www.suschem.org)) promoted from the European Federation of Chemical Industries (Cefic). A new initiative launched from Cefic/ETP SusChem regards the Public–Private Partnership (PPP) Sustainable Process Industry Through Resource and Energy Efficiency (SPIRE) [2].

The SPIRE PPP will be instrumental in addressing the Grand Societal Challenges defined within the EUROPE 2020 Agenda through the broad correlation that SPIRE has across various flagships initiatives (Innovation Union, Resource Efficient Europe, New Skills for New Jobs, and Industrial Policy for the Globalisation Era). The realization of SPIRE is seen essential in order to rejuvenate the European process industry base and make the paradigm shift of decoupling economic growth from resource impact. The European process industry is uniquely positioned to drive this initiative as it transforms raw material feedstock into intermediate and end-user products and thus sits at the core of every value chain. SPIRE research and innovation roadmap is aimed at realizing different ambitious objectives to achieve resource and energy efficiency. Between these, the objective of a reduction in fossil energy intensity of up to 30 % from current levels by 2030 through in particular a progressive introduction of alternative (renewable) energy sources within the process cycle should be highlighted.

CO<sub>2</sub> use is a core part of this SPIRE initiative, and to achieve the objective of introduction of renewable energy in the process cycle, but a full implementation of a visionary way to achieve complete circle recycling of CO<sub>2</sub> using renewable energy sources would require long time and continuity in the vision. In the meantime, capture and conversion of CO<sub>2</sub> to chemical feedstock could provide new route to a circular economy. For this reason, a CO<sub>2</sub> initiative was launched by Cefic [3] with the objective to integrate on a longer-term vision the aspects already included in the SPIRE roadmap. The final aim is to develop artificial leaves–type devices [4], able to use CO<sub>2</sub> (possibly directly captured from the air), sunlight, and water to produce in a tailored way chemicals and fuels. This is a multi-generational objective, requiring different intermediate steps and objectives to be implemented.

An intermediate strategic element to seize such opportunity consists in effectively introducing renewable energy in the chemical production chain through the innovative use of CO<sub>2</sub>. Presently, over 95 % of the industrial processes still use thermal energy. Electrical energy use in the chemical industry is still quite limited, although electrical energy is the main output of the actual renewable energy sources (with the exception of biomass conversion). This contribution shows how the conversion of CO<sub>2</sub> into feedstock for the chemical/process industry is the most efficient way to introduce renewable energy in this value chain and discusses the various options possible to proceed in this direction, in particular from the perspective of the state of the art of catalysis.

## ***1.1 The Use of Renewable Energy in Chemical Processes***

The introduction of renewable energy in the chemical production chain is a major issue still not sufficiently addressed, given its critical role in final carbon and environmental footprint. Biofuels are still under consideration as a possible route to ultimately inject solar energy into the energy supply system. Nevertheless, there are still many concerns regarding the life-cycle methods used to assess a positive impact on the reduction in GHG emissions and in the environmental impact [5, 6].

Besides biofuels, all methods based on the use of renewable energy source produce electrical energy as output. Hydropower, geothermal energy, and wind and solar energy (photovoltaic cells) are producing electrical energy. However, electrical energy does not integrate well into chemical production, except as utility. Nearly all the industrial chemical processes are based on the use of heat as the source of energy for the chemical reaction [7], apart from very few processes using electrical energy (e.g., chlorine and soda production). In the chemical sector, on average only 20 % of the input energy is used as electrical energy (including that generated onsite) to power the various process units and for other services [8]. This value nearly halves if we include that the feedstocks for the chemical sector are also derived mostly from fossil fuels. In the petroleum refining sector, only about 5 % of the input energy is used as electrical energy [9], and this value becomes few percentage if we consider the raw materials.

Solar thermal energy can be in principle coupled with a chemical reaction to provide the heat of reaction, but there are many technical problems for scaling-up this technology, between all the impossibility to maintain 24 h production and to guarantee uniform temperature during the day. Discontinuity of electrical energy production from wind, PV solar cells, etc. is a major drawback for the use of renewable energy in the chemical production which requires constant power supply. Therefore, to introduce renewable energy in the chemical production chain, it is necessary to convert renewable to chemical energy, by synthesizing molecules that can be easily stored and transported as well as that can be then used as raw materials in the chemical industry.

There are many social and political pushes to re-assess the way process industry uses renewable energy, between these the developments in renewable energy systems augmented by the renewable portfolio standards mandated in many states and countries, various energy conservation measures, the legislative climate, current and future taxation, limits on carbon emissions, other environmental and political concerns, etc. It is thus necessary to make an effective step forward in the development of effective ways by which renewable energy could be effectively integrated into the chemical production chain.

This paper, based largely on the more in-depth discussion made in Ref. [10], aims to show that the use of renewable energy to convert CO<sub>2</sub> to some valuable materials for chemical industry is an effective way to smoothly integrate renewable energy into the chemical production chain, while preserving the actual infrastructure and thus limiting the massive costs related to a change in the process

and raw materials as often necessary using alternative raw materials such as biomass. The chemical (re)use of CO<sub>2</sub> using renewable energy thus becomes a key aspect toward the more general goal of resource and energy efficiency, because it combines the reuse of a waste and of a relevant carbon sources to the reduction in fossil fuel use as well as GHG and pollutants emissions.

## 2 CO<sub>2</sub> (Re)use and Energy Vectors: Toward Solar Fuels

Different sources of renewable energy (solar, wind, tides, hydro, etc.) are currently used and have a large significance to grow further, even with some disparities. Actual fraction of renewable energy sources is still often limited to not eco-efficient options (such as wood combustion) or to routes whose further potential increase is close to limit (hydroelectricity). For other types of renewable energies, particularly solar energy, however, the potential is large.

The actual average global energy consumption is about 16 TW, and it is estimated to increase to about 25 TW by year 2050 [11]. A conservative estimation of the potential for solar energy is at least 5–10 times higher than this estimated consumption, while significantly lower for other renewable sources: 2–4 TW for wind, 2–3 TW for tides, 5–7 TW for biomass, and 3–6 TW for geothermal energy [12]. Of these different renewable energy sources, only biomass can be converted to liquid fuels and raw materials for chemical industry, while almost all the others produce electrical energy. Biomass, however, is quite complex, and producing fuels/chemicals in a sustainable and economic way is still a challenge, even considering the fast developments in this area. In addition, still several question marks exist on the effective contribution to GHG reduction and environmental impact of the massive use of biomass, as commented above.

Relevant progresses have been achieved over the last 5 years (2006–2011) in the introduction of renewable energy. The IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation [13] indicates that renewable energy capacity grew significantly in the last 2 years, despite global financial crisis. On a global basis, it is estimated that renewable energy accounted for 12.9 % of the total 492 Exajoules (EJ) of primary energy supply in 2008, but the largest RE contributor was associated with burning biomass (10.2 %). Hydropower represented 2.3 %, whereas other renewable energy sources accounted for 0.4 %. Renewable energy capacity continued to grow rapidly in 2009 compared to the cumulative installed capacity from the previous year, including wind power (32 % increase, 38 Gigawatts (GW) added), hydropower (3 %, 31 GW added), grid-connected photovoltaics (53 %, 7.5 GW added), geothermal power (4 %, 0.4 GW added), and solar hot water/heating (21 %, 31 GWth added).

While in some cases the rate of increase in the last years was quite high (wind and solar), the share of total energy production is still low. In these conditions, the electrical energy produced from renewable energy technologies could be given to the grid, but in the future, with an increasing share, it will be necessary to provide

continuity of the supply. On the other hand, even with the expected increase in the storage efficiency of advanced batteries [14], direct electrical energy storage of the batteries will continue to be a major limit in many applications. Actual society and energy scenario is largely based on the use as energy vector of liquid hydrocarbons, derived mainly from the refining of oil. Of the world energy final consumption, about 43 % is accounted by oil and derived liquid fuels (gasoline, diesel, jet fuels, gasoil, etc.) [11]. In contrast, only about 17 % is accounted by electrical energy, also due to the limit in energy storage. The specific energy of batteries, that is, their capacity for storing energy per kilogram of weight or the unit volume, is still only 1 % of the specific energy of gasoline.

Distribution of energy, matching time, and geographical demand with production capacities (wind and solar energies, the two renewable energies with higher rate of increase, are typically discontinuous), realize solutions for use of energy in mobile applications (from cars to laptops) are all pushing element to the development of effective solutions for energy storage and transport. The further development of a sustainable energy scenario requires finding efficient solutions to store and transport RE. Being the conversion of electrical to chemical energy still the preferable option, the issue is thus the development of the optimal energy vectors for renewable energy. This is the base concept of developing solar fuels [15–19]. Suitable energy vectors must fulfill a number of requirements. They should

- have both a high energy density by volume and by weight;
- be easy to store without need of high pressure at room temperature;
- be of low toxicity and safe in handling, and show limited risks in their distributed (non-technical) use;
- show a good integration in the actual energy infrastructure without need of new dedicated equipments;
- have a low impact on the environment in both their production and use.

H<sub>2</sub> could be an ideal energy vector [20–22] regarding many of these requirements, but the energy density of H<sub>2</sub>, even considering future possible developments in storage materials, will be still a main issue for practical large-scale use. A clear gap exists between both H<sub>2</sub> and electrical storage with respect to liquid fuels based on fossil or renewable (biomass) sources. In addition, its use requires large costs for a new energy infrastructure, and it does not integrate with the actual devices, thus not allowing a smooth transition. In terms of sustainability, the cost parameter is one of the critical elements. When a novel technology requires high costs to be introduced, it will take long time to be eventually applied. A solution which better integrates in the actual infrastructure is thus preferable, because it has a lower economical barrier for the introduction and may be applied in a shorter term.

Solar hydrogen may be a better and more sustainable alternative when combined with the possibility of forming liquid fuels easily transportable and with high energy density [23–25]. In addition, hydrogen is unsafe, in particular in transporting energy over long distances. The transformation of hydrogen into a safe transportable chemical is thus desirable for bulk energy transport.

Current energy vectors based on liquid fuels are fulfilling all the requirements for suitable energy vectors, except the last point, particularly regarding the emissions of greenhouse gases, because the available catalytic technologies can effectively minimize the emissions of the other pollutants produced during the combustion (particularly NO<sub>x</sub>). Although challenging, to find an efficient solution to (re)use the CO<sub>2</sub> produced during the combustion to form back fuels using renewable energy will be thus preferable and more sustainable than to develop new energy vectors and a new energy infrastructure. The CO<sub>2</sub> conversion to liquid fuels (methanol or other liquid chemicals) forms safe chemicals with high energy density, with minimal (and well-established) risks in storage, and this route may be well integrated with the existing energy infrastructure with minimal investments.

The techno-economic analysis reported in [Chap. 4](#) evidences that this is also a feasible option. Producing solar fuels via the (re)use of CO<sub>2</sub> is thus a carbon-neutral approach to store and transport solar energy (and of other renewable or no-carbon-based energy sources) which can be well integrated into the current energy infrastructure.

### 3 Power-to-Gas

Previous section has highlighted the issue of high daily and seasonal fluctuation in renewable energy production, and the problem that during off-peak periods the grid is not already able to accept a surplus of electrical energy. Today, wind turbines are stopped if the electricity generation is above the demand. For example, in Germany, 150 GWh of renewable, CO<sub>2</sub>-free, electricity got lost in 2010. This was an increase by 69 % compared to 2009. It is expected that the amount of lost electricity will be increasing with the further extension of highly volatile renewable energy supply. Furthermore, the electricity consumers are mostly located several hundred kilometers away from the renewable electricity production, for instance in the case of wind power. The necessary expansion of the electrical grid is a time-consuming and expensive task that also shows at the moment a low social acceptance. The conversion of surplus electricity into gas, which can be transported and stored in the vast network of gas pipelines and underground storage facilities throughout Europe, is an attractive option, since it provides solutions for both the necessary storage capacity, which can be even seasonal or long-term, and the energy transport over large distances at low losses. These are the basic motivations for the push, particularly in Germany but progressively extending to other countries such as Italy showing an increased production of renewable energy, for the so-called *power-to-gas* technology (P2G) for storage of renewable electricity in the natural gas infrastructure.

The current technology for the conversion of electricity into gas is based on the electrolysis of water to provide hydrogen used in the methanation of CO<sub>2</sub> to methane. Current efficiencies for the conversion step to hydrogen via electrolysis lie currently at a moderate level of ca. 70 %. The maximum efficiency of low

temperature electrolysis for large application to date is about 73 %. Combined with the maximum thermodynamic efficiency of methanation, which is about 83 %, the highest reachable process efficiency for the two processes executed in series is about 60 %. As already discussed in Chap. 1, there is thus the need to develop from one side better technologies for electrolysis (in particular, improving electrolyzers design and electrodes, and especially developing novel electrocatalysts not containing noble metals and with reduced overpotential in H<sub>2</sub> generation) and from the other side improve the catalysts for methanation reaction.

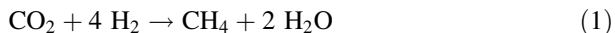
There is also the possibility of innovative solutions to improve the overall energy efficiency. An example is the coupling of high-temperature electrolysis and methanation to balance the exothermic and endothermic processes.

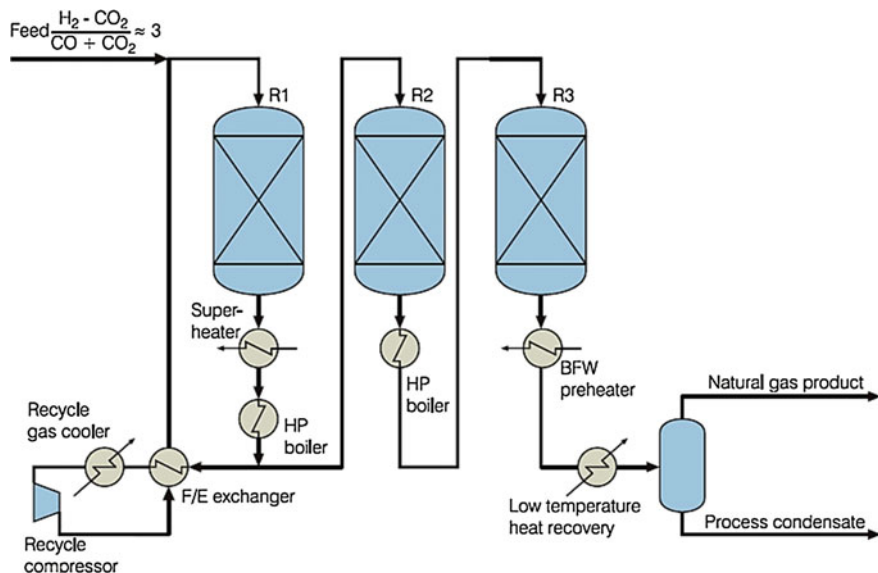
The reaction of CO<sub>2</sub> methanation is known from over a century (Sabatier reaction), but has received a renewed interest recently, for the use as chemical storage of the excess of electrical energy as pointed above [26]. A technology review of the production of synthetic natural gas (SNG) from coal and dry biomass was recently made by Kopyscinski et al. [27]. A number of companies have developed the process, typically at the pilot plant scale, but in relation to the production of SNG starting from biomass or coal. Haldor Topsoe TREMPTM technology (Topsøe's Recycle Energy efficient Methanation Process) was instead designed as an integrated cycle process of steam reforming of methane and methanation of the synthesis gas to store and distribute over long distance process heat from nuclear high temperature reactors [27]. The methanation plant consists of three adiabatic fixed bed methanation reactors (Fig. 1). The temperatures in the reactors range from 250 to 700 °C and the pressure up to 30 bar. Besides the complexity of having three reactors in series, with the last operating at high temperature, a progressive decrease in activity in the high-temperature methanation catalyst was observed [27].

Applying this technology to the P2G case would thus require developing improved methanation catalysts which (1) operate efficiently at low temperatures (<450 °C) and avoid the need to use three reactor in stage, (2) are more stable in long-term operations, (3) allow to use pure CO<sub>2</sub>, and (4) could be transferred to operations in microreactor, for the need to have compact-size devices for distributed applications. Therefore, even if large research has been made in the past on methanation, there is a number of new constraints which determine the need of a specific research.

Figure 2 shows the general integration of power-to-gas concept with the existing gas and electricity grids, the storage (underground) of natural gas, and the possible integration also with the mobility sector [26]. Solar electricity or any other type of renewable electricity can be integrated in the scheme.

Sabatier reaction is the hydrogenation of CO<sub>2</sub> to methane Eq. (1) requiring a 4:1 = H<sub>2</sub>:CO<sub>2</sub> ratio, thus higher than the conversion of CO<sub>2</sub> to formic acid, methanol, or FT products.





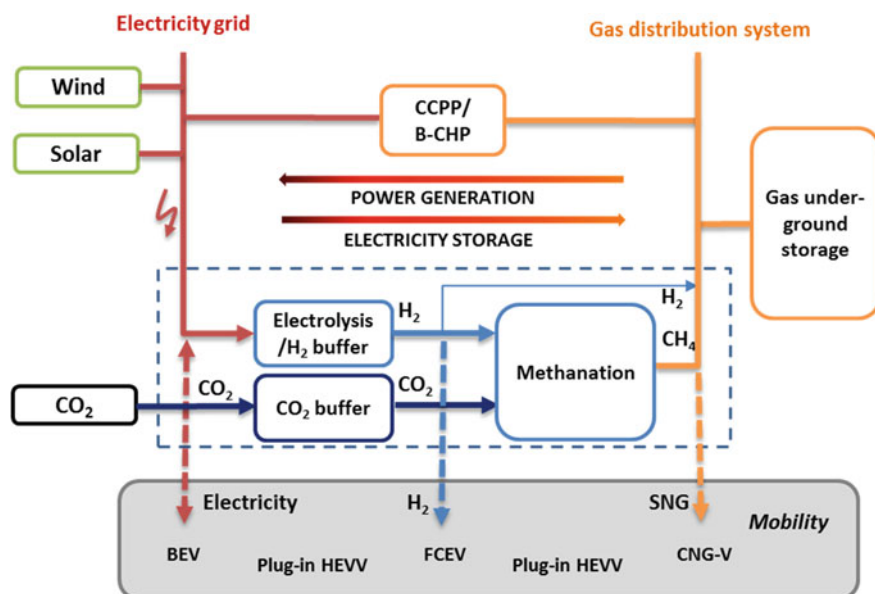
**Fig. 1** Schematic diagram of Haldor Topsoe's TREMP™ technology for methanation of syngas. Adapted from Ref. [27]

As mentioned above, there is the need to develop improved catalysts (active at lower temperatures) and suitable for the compact devices to be used for the electrical-to-energy conversion outlined in Fig. 2. Between the new constraints present are the need of a fast start and shutdown, the enhanced resistance to deactivation due to these fast cycling modes, and the need to be integrated into microreactors to develop compact devices for a distributed use.

The catalysts used have some similarities to those for  $\text{CO}_2$  reforming. 10 wt%Ni/CeO<sub>2</sub> shows a high  $\text{CO}_2$  methanation activity and high  $\text{CH}_4$  selectivity at low temperatures. Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (another good catalyst in reforming) shows also good performances in  $\text{CO}_2$  methanation at low temperatures [28]. There is a link between  $\text{CO}_2$  and CO methanation catalysts, the latter being often based on supported Ru catalysts [29].

The reaction mechanism for CO methanation includes both dissociative and associative reaction pathways [30]. The former, which dominates at lower reaction temperatures (typically <250 °C), involves hydrogenation of surface carbon produced by dissociative adsorption of CO, whereas the latter involves hydrogenation of CO species adsorbed at the metal-support interface. Dissociation of CO results in accumulation of adsorbed oxygen species at low temperatures. They cannot be removed from the catalyst surface, rendering catalyst inactive. Catalytic activity is restored at higher temperatures, where partially oxidized sites are reduced efficiently by adsorbed hydrogen atoms. The associative reaction pathway is the only one which is operable under conditions of  $\text{CO}_2$  methanation and proceeds via intermediate formation of carbonyl species at the metal-support interface,





**Fig. 2** Power-to-gas concept for bidirectional coupling of the electricity and gas grids with a link to the mobility sector. *Acronyms* B-CHP block-type combined heat and power station, BEV battery electric vehicle, CCPP combined cycle power plant, CNG-V compressed natural gas vehicle, FCEV fuel cell electric vehicle, Plug-In HEV plug-in hybrid electric vehicle. Reproduced with permissions from Ref. [10] (adapted from Ref. [26])

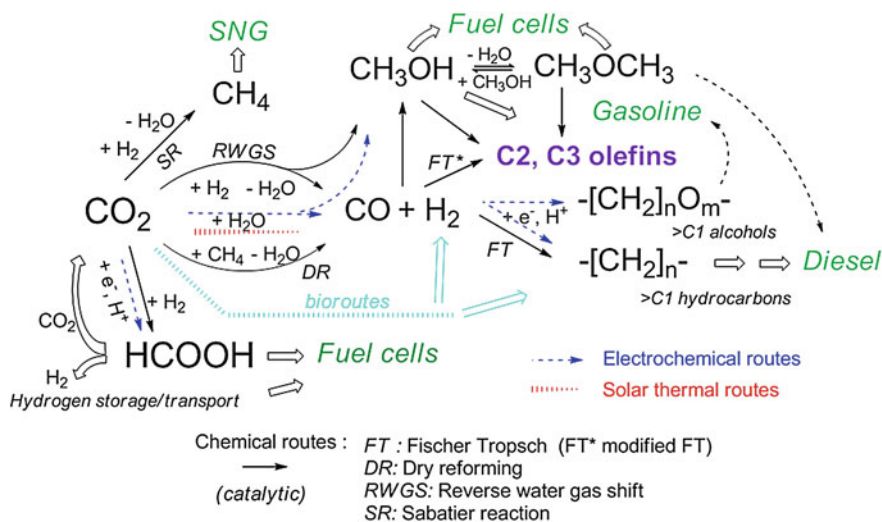
produced by the RWGS reaction [30]. Accordingly, Ru-doped ceria shows interesting performances in CO<sub>2</sub> methanation [31]. A conversion of 55 % of CO<sub>2</sub> with a 99 % selectivity for methane at a temperature of 450 °C was observed over Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> catalyst [31]. On Pd-MgO/SiO<sub>2</sub> catalysts, a bifunctional mechanism is instead present, with MgO initiating the reaction by binding CO<sub>2</sub> and forming a magnesium carbonate species on the surface which is then hydrogenated through spillover H species generated on Pd [32]. The performances of this catalysts at 450 °C are very comparable to those of the cited Ru-doped ceria (95 % selectivity to CH<sub>4</sub> at a carbon dioxide conversion of 59 %) [33].

Notwithstanding the different reaction mechanisms and characteristics of catalysts discussed above, there are thus analogous performances and the key elements for a significant improvement in the performances are not yet established. In this respect, it is useful to mention the recent observation [34] that on very narrow Ru particles supported on TiO<sub>2</sub> (mean diameter 2.5 nm), it is possible to realize the methanation of CO<sub>2</sub> with a 100 % yield at very low temperatures (ca. 160 °C), about 200 °C lower than a similar catalyst having a broader and larger Ru nanoparticles distribution. Particle size is thus a key parameter to control to develop highly active catalysts, although an effective mechanism must be found for the long-term stabilization of very small nanoparticles.

## 4 Routes for Converting CO<sub>2</sub>

An overview of the different possibilities and routes to convert CO<sub>2</sub> with specific reference to the issue of introducing renewable energy in the energy and chemical production chains is presented in Fig. 3. We may distinguish in this reaction network between routes relevant for the energy chain and those leading to raw materials for the chemical production chain, although in some cases (typical is methanol, but also DME—dimethylether) the product could be relevant for both cases. In this reaction network are considered only routes where the energy necessary to convert carbon dioxide to an higher-energy-level product derives in part, if not totally, from renewable energy sources. Routes to form products such as CO<sub>2</sub>-based polymers are not considered here. They are discussed in Chap. 1 together with the conversion of CO<sub>2</sub> to light olefins. The discussion on the latter will be not duplicated here, but it should be remarked that it is an important element in the possibility to introduce renewable energy in the chemical production chain, because light olefins are the raw base materials for petrochemistry. Figure 1 also indicates the possibility of using electrochemical or solar thermal routes to produce some of the chemicals reported in Fig. 1.

There are different possible energy vectors which derive from the hydrogenation of CO<sub>2</sub>, either directly or through the intermediate stage of the rWGS reaction:



**Fig. 3** Overview of the CO<sub>2</sub> conversion routes to incorporate renewable energy in the chemical and energy chains. The renewable energy is used either directly (in the solar thermal production of syngas) or indirectly, according to two main possibilities: (1) production of renewable H<sub>2</sub> or (2) production of electron, or electron/protons (by water photo-oxidation), used in the electrochemical routes [10]. Reprinted here with permission from ©Energy and Env. Science (2012)



to produce syngas (mixture of CO/H<sub>2</sub>) which can then be converted through the already-established (and commercially applied routes, although the syngas is produced from hydrocarbons instead from CO<sub>2</sub> and H<sub>2</sub>):

- formic acid, which may be used in formic acid fuel cells or as a vector to store and transport H<sub>2</sub> (the reaction of synthesis is reversible and formic acid can be catalytically decomposed in mild conditions to form back H<sub>2</sub> and CO<sub>2</sub> [25, 35]);
- methanol and dimethylether (DME)
- methane (substituted natural gas, SNG; see discussion in Sect. 3);
- >C1 alcohols or hydrocarbons.

Syngas may be produced also by reaction with hydrocarbons (particularly methane) through the so-called dry reforming (DR). The main potential advantage of this route is that it can be applied directly to flue gases (even if technical problems exist), while all the other routes require a first step of separation of CO<sub>2</sub> from the flue gases. However, DR is an endothermic reaction occurring at high temperature (about 900–1,000 °C) and with formation of carbon (which deactivates the catalyst) as a side reaction. The reaction may be combined with the wet reforming of methane (with H<sub>2</sub>O) and its partial oxidation (the so-called dry-reforming) [36].

The catalytic chemistry of rWGS reaction and the following transformation to methanol/DME, or hydrocarbons via Fischer–Tropsch, and the subsequent production of gasoline (methanol-to-gasoline, MTG) or of diesel via hydrocracking of the alkanes produced in FT process (using Co-based catalysts) is well established, even if there is still need of development, due to the change in feed composition starting from CO<sub>2</sub> than from syngas. Also in terms of process development, most of the knowledge necessary is available. Minor technological barriers to develop these routes are thus present. Only for the synthesis of formic acid, either catalytically or electrocatalytically, there is still need of development in terms of productivity and stability.

The main gap in the catalytic routes of CO<sub>2</sub> conversion to fuels is economic, with the cost of production of renewable H<sub>2</sub> as the key factor. However, already opportunities exist in terms of available (low-cost) sources of renewable H<sub>2</sub> which make interesting the production of fuels from CO<sub>2</sub> (see also Chap. 4). Mitsui Chemicals and Carbon Recycling International are two companies which are running pilot plant projects to exploit the conversion of CO<sub>2</sub> to methanol, while Mantra Venture Group and DNV are exploring at pilot plant scale the electroreduction of CO<sub>2</sub> to formic acid. RCO2 AS has instead developed at pilot scale a process based on recovery of CO<sub>2</sub> from flue gas and its conversion to methane using renewable H<sub>2</sub>. Details on these processes and the related chemistry and catalysis are discussed elsewhere [37, 38]. A book discussing the various possible routes for CO<sub>2</sub> conversion was recently published from Aresta [39]. Other authors have also recently published reviews recently on this topic [40–44].

The catalytic synthesis of higher alcohols from CO<sub>2</sub> is an interesting route, but still not competitive. New interesting catalysts, however, have been developed. Conversion of CO<sub>2</sub> to higher alcohols and hydrocarbons ( $\geq$ C<sub>2</sub>) using biocatalysis or electrocatalysis methodologies is also an interesting route, but still at preliminary stage [15, 16]. Genetically modified cyanobacteria have been recently reported to consume carbon dioxide in a set of steps to produce a mixture of isobutyraldehyde (primarily) and isobutanol. Using a gas phase electrocatalysis approach, CO<sub>2</sub> may be reduced to a mixture of  $\geq$ C<sub>2</sub> hydrocarbon and alcohols, mainly isopropanol [40]. Artificial metabolic pathways involving enzymes or cyanobacteria have been proposed to use NADPH and ATP from photosynthesis for the synthesis of n-butanol (UCLA) or isobutene (Global Bioenergies) directly from carbon dioxide and water.

The conversion of CO<sub>2</sub> to hydrocarbons and alcohols using radiations and/or electrons (photo-, electro-, or photoelectro-catalytic methods) is actively investigated worldwide with the aim to develop non-biomimetic artificial leaves which use solar light, CO<sub>2</sub>, and water to make directly solar fuels. Even if impressive results have been reported recently, it is still a long-term solution for the still low productivities. It is also evidenced that often are unclear the intrinsic barriers for practical applications on the investigated routes, and it is thus necessary to better focus on the research. Details are discussed elsewhere [15, 16, 41].

## 5 Producing Renewable H<sub>2</sub>

The availability of renewable H<sub>2</sub> at enough low cost to make economically sustainable the production of the chemicals and fuels indicated in Fig. 3 is the prerequisite to enable a CO<sub>2</sub> economy today, while in the future, as outlined in Chap. 1, the generations of active hydrogen (e.g., protons and electrons) could be produced integrated in the device for CO<sub>2</sub> conversion. Today, however, the maturity of H<sub>2</sub> production routes, their respective GHC impact, and their costs are key aspects to assess the possibility of renewable energy injection in the energy/chemical production chains through CO<sub>2</sub> recycling.

### 5.1 Current Status

There is a large effort in producing H<sub>2</sub> from biomass sources [42]. Although this type of processes are often considered part of the possibilities to produce renewable H<sub>2</sub>, not enough attention it is given in general to assess the sustainability of biomass-based processes [43]. H<sub>2</sub> may be produced from biomass-derived products through different methods [6], either via aqueous phase catalytic reforming [44, 45] or through thermocatalytic methods [42, 46], but due to both the impact of biomass cultivation on GHG emissions and the significant energy consumption in the

harvesting, transport, and processing biomass, the net impact on GHG emission per mole of  $H_2$  is significant, although lower than from fossil fuels.

Methane steam reforming is the main current commercial method to produce  $H_2$  [47]. Four moles of  $H_2$  are produced per mole of  $CO_2$ , that is, 5.5 kg  $CO_2$  per kg  $H_2$ , but considering the life-cycle of production, this value rises to about 8.9 kg  $CO_2$ /kg  $H_2$  [48]. Estimation of the amount of  $CO_2$  produced per kg of  $H_2$  starting from biomass should include in the life-cycle assessment (LCA) many aspects difficult to evaluate, from the growing of biomass (including the GHG impact deriving of the use of fertilizers, land change uses, etc.) to biomass harvesting/transport, conversion, and related technologies/routes utilized. Still fully reliable estimations do not exist or are highly depending on the specific case. On the average, the estimated value is about 5–6 kg  $CO_2$ /kg  $H_2$  [49, 50].

For the production of  $H_2$  using direct renewable energy sources, the current most consolidated methodology is to produce electrical energy using photovoltaic panels, wind turbines, or other similar options (geothermy, waves, etc.), and then use an electrolyzer. LCA data are not reliable, because all technologies are still at the stage of development. For wind/electrolysis, a value below 1 kg  $CO_2$ /kg  $H_2$  was estimated [51]. Utgikar and Thiesen [52] reported life-cycle  $CO_2$  emissions for various hydrogen production methods and indicated values for  $H_2$  from hydroelectric/electrolysis or solar thermal around 2 kg  $CO_2$ /kg  $H_2$ . Higher values (around 6  $CO_2$ /kg  $H_2$ ) were reported for the photovoltaic (PV)/electrolysis combination, but this estimation was based on an old PV technology. Taking into consideration the fast progresses in the field, a more reasonable estimation is 1–2 kg  $CO_2$ /kg  $H_2$ .

Therefore, the direct routes of producing renewable  $H_2$  have an impact on  $CO_2$  emissions about one-third of that of producing renewable  $H_2$  from biomass conversion routes and about one-fifth that of current methods to produce  $H_2$ . Being this step of producing renewable  $H_2$  the most relevant in terms of energy accounting for the entire process of conversion of  $CO_2$  to chemicals by hydrogenation, it is evident that direct methodologies using renewable energy to produce  $H_2$  are preferable to those through the use of biomass.

A detailed discussion on the cost of production of renewable  $H_2$  has been already reported [10, 53]. Modern electrolyzers produce  $H_2$  under pressure, differently from other routes, and this is a relevant cost advantage. However, still high-pressure electrolyzers are not reliable in terms of long-term stability. PEM water electrolysis technology is considered today the safer and preferable way to produce renewable  $H_2$ . Stack efficiencies close to 80 % have been obtained operating at high ( $1\text{ A cm}^{-2}$ ) current densities using low-cost electrodes and high operating pressures (up to 130 bar) [54, 55]. Between the advantages of PEM electrolyzers over the well-established alkaline technology, the absence of corrosive electrolytes and the better integration with solar and wind power may be cited. Recent developments in terms of catalyst optimization, optimized design of electrolyzer cell, and cost reduction of the membrane-electrode assembling have already led to a significant stack capital cost reductions. A still relevant problem to

solve is how to reduce the overpotential in  $H_2$  production, but this will require a better understanding of the fundamental aspects of the reaction mechanism.

In terms of cost, it is possible to produce  $H_2$  by combining wind power and PEM electrolyzers at about 3 \$/kg at the best, with an average cost in the 4–6 \$/kg. When cheap electrical energy sources (or unused electrical energy during night, for example) are available, cost can be even lower, as discussed in [Chap. 4](#). Current production is still on small scale, and it is still difficult to predict the possibility of larger scale production of  $H_2$  using electrolyzers, including possible scale-economies. Together with the improvements in technology of production of renewable energy and of electrolyzers, it is likely to produce  $H_2$  at a cost below about 4–5 \$/kg  $H_2$  in a near future.

Using a combination of solid oxide electrolysis cells (SOEC) and thermal solar technologies, it is also possible to produce renewable  $H_2$  at competitive costs. For low temperature electrolysis, a larger quantity of electrical energy is necessary to overcome the endothermic heat of reaction, while at high temperatures the primary electric energy demand is considerably reduced, and the electrical losses in the cell decrease due to lower ohmic resistance in the electrolyte and lower polarization losses from the electrode reactions, being the kinetics of the electrolysis reactions faster.  $H_2$  cost from high-temperature electrolysis has been estimated in the 1.5–2.6 \$/kg  $H_2$  range [\[56\]](#), although it appears an optimistic estimation.

## 5.2 Ongoing Activities to Establish New Sustainable Routes

There are various novel routes to produce renewable  $H_2$  which are under active investigation:

- *Bio- $H_2$* : producing  $H_2$  through the use of cyanobacteria [\[57\]](#) and other bacteria [\[58\]](#);
- *Photocatalytic routes*: using different type of semiconductors, particularly those active with sunlight [\[59, 60\]](#);
- *Microbial* electrolysis [\[61\]](#);
- High temperatures approaches [\[62, 63\]](#).

All these routes are attractive and under active research. More details are discussed in Ref. [\[15, 41\]](#). However, they are still under development and with many uncertainties to assess their techno-economic feasibility. Furthermore, productivities are still quite low. Their potential was estimated to become quite large (over 1 billion metric tons of hydrogen annually in US) in less than two decades [\[64\]](#), but estimation is probably optimistic, even if it remarks the need to further stimulate the R&D in this field.

## 6 Conclusions

This paper has presented the concept of how the conversion of CO<sub>2</sub> through the use of renewable energy sources offers new possibilities to develop innovative new approaches to improve sustainability of the chemical and energy production. This topic is a key component for the strategies of chemical and energy industries (particularly in Europe), in terms especially of addressing resource and energy efficiency.

In the previous paper, it was already discussed how, for example, CO<sub>2</sub> could be not only a valuable carbon source to produce polymers, but also a base raw material for the whole chemical sector, for example ethylene and propylene.

In this process, the renewable energy used to produce these raw materials is incorporated in the chemical production value chain. This is an efficient procedure to improve resource efficiency and limit greenhouse gas emissions.

We have shown here that there are different additional possibilities to proceed in the same direction, producing methanol or other alternative chemicals. Some of these represent a trade-union with the energy production chain, where the (re)use of CO<sub>2</sub> could also play the important role of establishing effective paths to store and transport renewable energy. Solar fuels and power-to-gas are two of the novel concepts in this area which remark the need to proceed in better establishing these routes, determine priorities, and start the seeds for a CO<sub>2</sub> economy. Developing effective energy vectors for the storage of solar energy and which integrates into existing energy infrastructure to allow a smooth, but fast transition to a more sustainable energy future is thus an important area to remark.

These examples show that it is possible to create a CO<sub>2</sub>-based and resource-efficient chemical and energy production. It is thus possible to expand current view of considering CO<sub>2</sub> as a valuable resource only for targeting high-value products, which, however, cannot significantly contribute to the recycle of carbon dioxide and the creation of a low-carbon economy. It is also evident that the discussed processes can be an enabling factor for an effective introduction of renewable energy into the chemical production chain, and the push toward solar fuels an effective driving force toward a more sustainable energy.

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