

Review

Recent Advances on CO₂ Mitigation Technologies: On the Role of Hydrogenation Route via Green H₂

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Abstract: The increasing trend in global energy demand has led to an extensive use of fossil fuels and subsequently in a marked increase in atmospheric CO₂ content, which is the main culprit for the greenhouse effect. In order to successfully reverse this trend, many schemes for CO₂ mitigation have been proposed, taking into consideration that large-scale decarbonization is still infeasible. At the same time, the projected increase in the share of variable renewables in the future energy mix will necessitate large-scale curtailment of excess energy. Collectively, the above crucial problems can be addressed by the general scheme of CO₂ hydrogenation. This refers to the conversion of both captured CO₂ and green H₂ produced by RES-powered water electrolysis for the production of added-value chemicals and fuels, which are a great alternative to CO₂ sequestration and the use of green H₂ as a standalone fuel. Indeed, direct utilization of both CO₂ and H₂ via CO₂ hydrogenation offers, on the one hand, the advantage of CO₂ valorization instead of its permanent storage, and the direct transformation of otherwise curtailed excess electricity to stable and reliable carriers such as methane and methanol on the other, thereby bypassing the inherent complexities associated with the transformation towards a H₂-based economy. In light of the above, herein an overview of the two main CO₂ abatement schemes, Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU), is firstly presented, focusing on the route of CO₂ hydrogenation by green electrolytic hydrogen. Next, the integration of large-scale RES-based H₂ production with CO₂ capture units on-site industrial point sources for the production of added-value chemicals and energy carriers is contextualized and highlighted. In this regard, a specific reference is made to the so-called Power-to-X schemes, exemplified by the production of synthetic natural gas via the Power-to-Gas route. Lastly, several outlooks towards the future of CO₂ hydrogenation are presented.

Keywords: carbon capture and utilization; green H₂; CO₂ hydrogenation; power-to-X



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1. Introduction

Energy is indisputably the most valuable commodity in modern society. It is omnipresent and comes in many different forms (e.g., chemical, mechanical, thermal, electrical, nuclear), but not all types of energy can be directly exploited in order to meet our vast and ever-increasing demands, due to the intensification of anthropogenic activities and the continuous rise in global population. The rise in global population since 1950 and United Nations (UN) projections until the end of the 21st century are depicted in Figure 1 [1]. Additionally, in a society that is increasingly advancing technologically, resource availability will be inevitably limited in the short-to-medium term due to the increasingly higher demands. The calculations by the International Energy Agency (IEA) show that the total energy demands globally in 2018 were approximately 10 Gtoe or ~116 GWh (1 toe is conventionally

defined as the energy amount released by burning 1 tonne of crude oil) and they present an upward trend. Indicatively, the energy in 1990 was ~6.4 Gtoe (~74 GWh), showcasing an increase of 36% in roughly three decades. On the other hand, the estimated primary energy consumption per capita remains relatively stable for the period 1990–2018, ranging between 1.6–1.9 toe per capita [2].

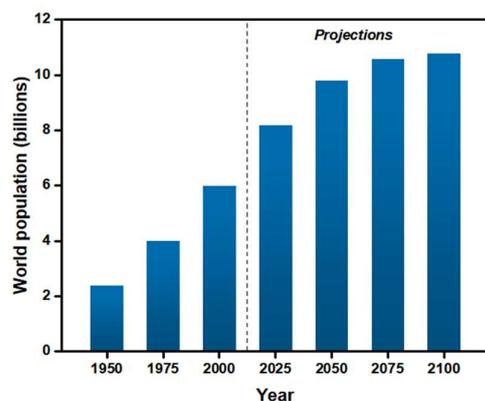


Figure 1. Evolution of global population since 1950 and projections until 2100. Created by the authors using data from the United Nations [1].

The role of the energy sector is very important in terms of wealth increase and subsequently for national growth and also in terms of social and environmental sustainability. The satisfaction of the needs of our society by simultaneously safeguarding the environment and enabling future generations to prosper on the Earth is one of the utmost significant challenges on a global scale. Thus, it becomes evident that new solutions are urgently needed in order to sustain the standard of living of the developed world. The aforementioned energy load values are unprecedented and are met today by the utilization of only relatively few energy sources and sectors, evidenced by the sector-divided energy consumption values in Table 1, using data from the International Energy Agency [2]. It can be seen that, since 1990, the industrial, transport and residential sectors consistently account for more than 70% of the total consumption, whereas the total consumption has increased steadily in absolute terms, in accordance with the rise in global population (Figure 1).

Table 1. Global energy consumption by sector between 1990–2018.

Sector	Gross Final Consumption by Sector in Gtoe (% of Total)			
	1990	2000	2010	2018
Industry	1.80 (28.8)	1.86 (26.6)	2.63 (29.9)	2.83 (28.6)
Transport	1.57 (25.2)	1.96 (27.9)	2.42 (27.5)	2.88 (29.1)
Residential	1.53 (24.4)	1.80 (25.6)	1.98 (22.5)	2.10 (21.2)
Commercial and public services	0.45 (7.2)	0.56 (8.0)	0.72 (8.1)	0.80 (8.2)
Agriculture and forestry	0.16 (2.6)	0.15 (2.1)	0.18 (2.0)	0.20 (2.1)
Not specified	0.26 (4.2)	0.08 (1.1)	0.11 (1.2)	0.14 (1.5)
Non-energy use	0.48 (7.7)	0.60 (8.7)	0.76 (8.7)	0.92 (9.3)
Total	6.25	7.01	8.80	9.87

Created by the authors using data from the International Energy Agency [2] (1 toe \approx 41.87 GJ).

In addition to the evident issue of the depletion of fossil fuel resources on our planet, another major problem stemming from the extensive fossil fuel usage in the energy mix is that upon combustion they eventually transform their carbonaceous matter into carbon dioxide. The correlation between the atmospheric CO₂ content and air temperature, known now as the greenhouse effect, was first suggested by Joseph Fourier two centuries ago and was proven by Svante Arrhenius at the end of the nineteenth century [3]. Nowadays, the unequivocal scientific consensus is that increasing CO₂ content in the atmosphere is the main factor contributing to global warming, as CO₂ is the gas exerting the highest

impact on the greenhouse effect due to its high concentration and ability to absorb and emit infrared radiation. Towards the goal to effectively mitigate the CO₂ emissions and climate change, a vast amount of resources and scientific research interest have been driven towards developing global-scale schemes to substantially reduce carbon dioxide content in the atmosphere, either by the gradual shift towards a non-fossil fuel economy dominated by renewable energy sources or by the direct capture [4–7] and/or eventual utilization [4,8–11] of the industrial CO₂ emissions or atmospheric CO₂ that cannot be realistically avoided within the relevant time frame.

Moreover, the increasingly higher share of renewables in the future decarbonized energy mix, as set out in several intergovernmental papers (e.g., the European Green Deal) is expected to lead to large amounts of sustainable energy input in the EWh range [12,13]. Provided that the large-scale deployment of electricity storage via accumulators and batteries will continue to be considered as a bottleneck owing to high costs and other practicalities [14] as well as the inherently intermittent nature of solar/wind energy provision due to meteorological fluctuations, it becomes clear that a means of curtailment of excess electricity provided by variable renewables at higher scales needs to be implemented. In this sense, the use of this excess power for large-scale hydrogen production via water electrolysis is becoming more attractive, since H₂ is a highly energetic molecule that is expected to hold a key role in the decarbonization of key industrial sectors and energy generation [15–19]. In this perspective, EU plans to install between 13–56 GW of electrolyzer capacity to cover the estimated hydrogen demand in the low and high scenarios, respectively [20]. Even more importantly, the combination of mass-produced electrolytic H₂ by the surplus of renewable energy at times of reduced electricity demand and/or increased electricity generation with a CO₂ stream stemming from large-scale CO₂ capture units can potentially provide a solution to both sufficiently address the curtailment of variable renewables and the valorization of CO₂ emissions. Essentially, this approach can potentially integrate the transformation of CO₂ emissions and unstable energy loads to valuable chemical commodities and/or gaseous/liquid fuels that may be characterized by a markedly reduced (or even net zero) carbon footprint compared to their conventional production paving the way towards climate neutrality [11,21–24].

Considering the above, in the present work, a collective overview of the proposed CO₂ mitigation schemes is presented, focusing particularly on the hydrogenation route via the environmentally friendly production of H₂. Specifically, the layout of the review is as follows:

1. Brief description of the detrimental role of CO₂ as the main greenhouse gas in climate change and directives towards CO₂ mitigation;
2. Summary of the two main CO₂ valorization routes, i.e., Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU);
3. Details on the route of CO₂ hydrogenation pathways via the exploitation of renewable energy sources for “green” H₂ production, the so-called “Power-to-X, PtX” processes, exemplified by “Power-to-Gas, PtG”;
4. Conclusions and future outlooks for the large-scale deployment of CO₂ hydrogenation schemes by electrolytic hydrogen.

2. The Past, Present and Future Role of CO₂

Upon a closer look at the energy mix in Table 1, it can be revealed that by comparing present values with those from the previous three decades, the distribution of the different primary energy sources in the energy mix is only slightly altered. Moreover, similar trends regarding energy sector shares in primary energy consumption are demonstrated when considering the same indicators for the EU28 region in 2018 (Figure 2). On the other hand, and according to IEA, energy supply at a global level is still dominated by non-renewable sources (i.e., coal, oil and natural gas), as seen in Table 2.

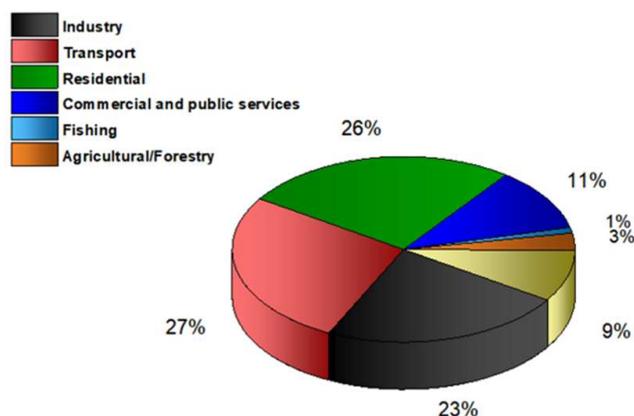


Figure 2. Breakdown of the EU28 final energy consumption in 2018 by sector. Created by the authors using data from the International Energy Agency [2].

Table 2. Global energy supply and electricity generation by source for 1990–2018.

Energy Source	Total Energy Supply in Gtoe (% of Total)			
	1990	2000	2010	2018
Coal	2.22 (25.3)	2.33 (23.1)	3.65 (28.4)	3.84 (26.9)
Oil	3.23 (37.0)	3.67 (36.4)	4.13 (32.1)	4.50 (31.5)
Natural gas	1.66 (18.8)	2.10 (20.9)	2.74 (21.3)	3.26 (22.8)
Nuclear	0.53 (6.0)	0.68 (6.8)	0.72 (5.6)	0.71 (5.0)
Hydro	0.18 (2.1)	0.22 (2.2)	0.30 (2.3)	0.36 (2.5)
Biofuels and waste	0.90 (10.3)	1.01 (10.0)	1.21 (9.4)	1.33 (9.3)
Wind, solar, etc.	0.04 (0.5)	0.06 (0.6)	0.11 (0.9)	0.29 (2.0)
Total	8.76	10.07	12.86	14.29
Electricity source	Total electricity generation in 10 ⁶ GWh (% of total)			
	1990	2000	2010	2018
Coal	4.43 (37.4)	5.99 (38.7)	8.66 (40.3)	10.16 (38.1)
Oil	1.32 (11.1)	1.18 (7.6)	0.97 (4.5)	0.78 (2.9)
Natural gas	1.75 (14.8)	2.77 (17.9)	4.84 (22.5)	6.15 (23.0)
Nuclear	2.01 (17.0)	2.59 (16.7)	2.76 (12.8)	2.71 (10.2)
Hydro	2.19 (18.5)	2.70 (17.5)	3.54 (16.5)	4.33 (16.2)
Biofuels and waste	0.12 (1.0)	0.14 (0.9)	0.29 (1.3)	0.65 (2.4)
Wind	0.02 (0.2)	0.04 (0.3)	0.34 (1.6)	1.27 (4.8)
Solar/Geothermal	0.01 (0.1)	0.06 (0.4)	0.09 (0.4)	0.64 (2.4)
Total	11.85	15.47	21.49	26.69

Created by the authors using data from the International Energy Agency [2] (1 toe \approx 41.87 GJ).

Further breakdown of the values for total energy consumption and supply per geographical region in the same period can be found in the recent review by Ahmad and Zhang [25]. It is noteworthy that energy generation based on fossil fuels accounts for at least 3/4 of the total energy supply, with absolute values presenting a steadily increasing trend. In addition, electricity generation is a significant metric of social and economic development and thus a very important indicator for the energy mix assessment. In general, it covers different types of energy resources and economy levels, and the energy development plan and energy consumption policy of a given country. Notably, it is seen that despite the recent progress in the increase in electricity technologies based on renewable energy sources (RES), current social and economic barriers continue to hamper the large-scale integration of renewable energy sources [9,26] and their penetration in the electricity generation sector remains less than a quarter of the total production.

Reducing emissions in the industrial sector is one of the most significant challenges towards achieving carbon neutrality. Combustion of natural gas emits ca. 50–60% less CO₂ with respect to coal and its share in the global primary energy consumption had thus been increased by 40% by 2020 and by the year 2030 a further increase of 15% compared to

2020 values is projected [25], unless other political factors restrain its expanded use. This is currently the case with the recently announced REPower EU plan, aiming to rapidly reduce dependence on Russian fossil fuels and fast-forward the green transition [27]. Additionally, the use of oil and coal will be significantly reduced but will still be a significant fraction of the energy conversion sector throughout the world.

However, as mentioned earlier, the increased use of fossil fuels has inevitably led to a substantial increase in the content of CO₂ in the atmosphere, since it is largely generated upon carbon-based fuel combustion. Whereas carbon dioxide is indeed the most prominent gas regarding the exacerbation of the greenhouse effect, other important greenhouse gases (GHGs) include primarily CH₄ as well as N₂O and several fluorinated gases (Figure 3), namely Chlorofluorocarbon-12 (CFC-12), Hydrofluorocarbon-23 (HFC-23), SF₆ and NF₃ [28]. Methane is largely considered to be the second most potent greenhouse gas after CO₂, given its increasing atmospheric concentration by the fact that it is emitted naturally as well as anthropogenically by a variety of sources [29,30]. Contribution of each gas to the greenhouse effect is in general assessed by a combination of metrics; atmospheric concentration, average lifetime in the atmosphere and specific infrared radiation adsorption capacity. The latter two are combined in the Global Warming Potential (GWP) index, which measures the total energy absorbed by a gas over a given time period (usually a century) relative to the emissions of 1 tonne of CO₂ [31].

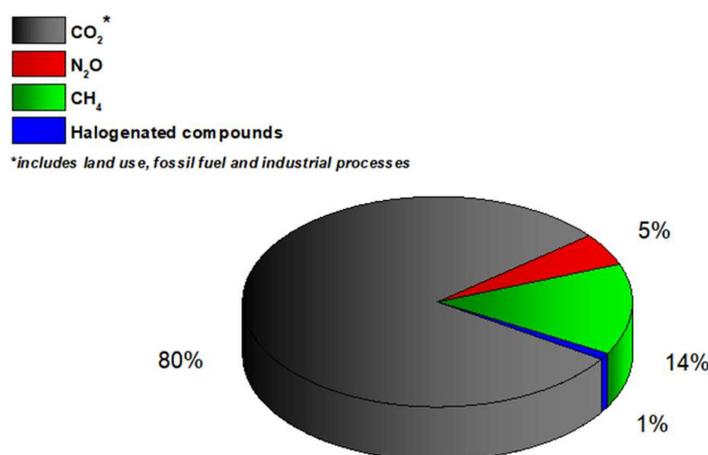


Figure 3. Relative contributions of gases to the greenhouse effect. Created by the authors using data from [28].

As for CO₂, the Earth has, in general, two major carbon reservoirs, carbon rocks and organic-rich rocks, practically containing the entirety of the carbon content of the planet. Notably, anthropogenic CO₂ emissions stem from the aforementioned reservoirs, either directly via the combustion/oxidation of carbon-containing fossil fuels from organic-rich rocks or semi-directly via the thermally induced splitting of carbonate minerals (predominantly limestone) from carbon rocks in the cement industry [32]. Ergo, carbon dioxide is omnipresent in the Earth's atmosphere, with a variety of sources contributing to its increasing atmospheric content. Different anthropogenic activities, such as transportation, electricity generation and industrial activities can be reasoned to be the main causes for the exceedingly high amounts of carbon dioxide emissions, a breakdown of which by each source is given in Table 3, using data from the work by Rafiee et al., [33].

Table 3. Anthropogenic sources of CO₂ emissions.

Sector	Annual Mtonnes of CO ₂ (% of Total)
Electricity and heat production	13.7 (42.4)
Transportation	7.4 (22.9)
Manufacturing industries and construction	6.1 (19.0)
Residential	1.9 (5.7)
Services	0.9 (2.8)
Other (agriculture/forestry, energy industries other than electricity and heat generation, marine and aviation bunkers, fishing)	2.3 (7.2)
Total	32.3

Created by the authors using data from [33].

Elsewhere, Gaffney et al. [34] have recently reported an estimation that anthropogenic emissions are responsible for climate change at a rate 170 times higher than that induced by naturally occurring phenomena. This is directly associated with the fact that since the onset of industrialization, global CO₂ emissions have skyrocketed, attributed to the dramatic increase in the use of coal and other fossil fuels that drove the economic development of the modern world. This has significantly disrupted the natural carbon cycle that had been established over millions of years until the industrial era [35].

According to numerous reports, CO₂ content increased up to 40% between 1750 and 2011 (an increase from approximately 280 to 390 ppm). Alarmingly, almost half of the total carbon dioxide emissions have occurred within the last 50 to 60 years, as the rate of CO₂ release until the 1960s had increased with less than 1 ppm per annum and more than doubled afterwards [33]. Additionally, as the global economy is still heavily reliant on the burning of fossil fuels and given that 1 tonne of fossil fuel releases more than 3.5 times an equivalent mass of CO₂, emissions are only projected to maintain this increasing trend. By the start of the 21st century, atmospheric CO₂ content approached the teratonne landmark [36]. This will subsequently lead to an increase in the overall temperature of the planet, as the IPCC has predicted an average global rise in temperature of about 1.5 until 2052 or even 5.8 °C by 2100 [37,38].

Collectively, the above stark conclusions are accentuated by the newly published Sixth Assessment Report of the IPCC, characteristically evidenced by the annual average CO₂ and CH₄ concentration values of 410 ppm and 1866 ppb, respectively, in 2019 [39]. This extensive and elaborate report essentially contains all the necessary information that one may need in order to fully grasp the extent to which the climate of the Earth has changed over the last centuries and the rather ominous conclusions with regard to its effects on the prosperity of human life in the near and far future. It must be mentioned that the IPCC is a globally recognized body responsible for tracking climate change and consists of a very large number of scientists and policymakers from a wide array of scientific fields pertinent to global climate. Thus, the interested reader may refer to the aforementioned report for detailed information and further reading. However, in an attempt to oversimplify for the purposes of this review, the most prominent conclusions of the IPCC's report can be summarized as follows:

- Global surface temperature was approximately 1.1 °C higher in the second decade of the 21st century than between the period 1850–1900, and the last five years in particular were recorded as the hottest since 1850.
- The latest sea level rise rate has increased by nearly threefold compared to the period 1901–1971 and sea levels have increased by ca. 80 cm.
- Acidification of the oceans has intensified, as the current oceanic pH value is estimated at 7.65, compared to the value of 8.10 in the 1960s.
- The observed warming stems from anthropogenic emissions, with greenhouse gas warming masked in part by the effect of aerosol cooling.
- Human influence is indeed “very likely” the main cause of the global retreat of glaciers globally since the 1990s as well as the decrease in Arctic sea-ice.

- It is “virtually certain” that hot and extreme phenomena (mostly heatwaves) have become increasingly more frequent and more intense since 1950, whereas cold events follow the opposite trend.

3. Directives and Global Goals towards Carbon Neutrality

The energy performance is undoubtedly one of the main pillars supporting every policy that aims to ensure the establishment of a sustainable and inclusive financial growth. Indeed, energy is a key (or even the most significant) factor towards meeting the global sustainability agenda and should therefore be the primary challenge for both developed and developing countries. Given the largely detrimental environmental and socio-economic impacts of global warming caused by the increasing CO₂ levels in the air, there has been a great amount of worldwide interest in recent decades in reducing and/or reversing this phenomenon. Citing again the main results from the IPCC’s Sixth Assessment Report [39], and regardless of the different future CO₂ emission scenarios examined, the most significant points regarding projections of the planet’s climate can be summed up in the following:

- Surface temperature globally is not expected to decrease until at least 2050. A global warming extent of 1.5 °C and 2 °C will be exceeded during this century, provided that deep reductions in emissions of CO₂ and other GHGs do not take place soon.
- Several climate system changes will become more prominent, directly ascribed to the increasing global warming. These changes include increased frequency and intensity of hot extremes, heavy precipitation and marine heatwaves, ecological/agricultural droughts in some regions and intense tropical cyclones, as well as Arctic sea-ice reduction, permafrost and snow cover.
- The sustained global warming is projected to further intensify the water cycle, specifically its variability, the severity of wet/dry weather phenomena and monsoon precipitation.
- Under scenarios with increased CO₂ atmospheric content, land and ocean carbon sinks are expected to be less effective at decelerating the accumulation of atmospheric CO₂.
- A lot of changes attributed to past and future trends regarding greenhouse gas emissions are now irreversible at a time frame between centuries or even millennia, especially changes in global sea level, ocean and ice sheets.

So far, the proposed policies and in turn the actions taken have not managed to reverse the trends in the past carbon dioxide emissions and the time for avoiding dangerous levels of global warming is now, more than ever, of the essence, since humanity is moving ever closer to reaching midnight in the Doomsday clock. Nevertheless, in a historic first, both developed and developing countries have initiated processes on a national scale in order to prepare plans for integrated climate and development for submission to the United Nations Framework Convention on Climate Change (UNFCCC). This is definitely an encouraging sign, suggestive of an initial co-operation and planning between countries with regard to implementing the global transition towards the protection of the planet’s climate [40].

Historically, treaties such as the Kyoto Protocol and the Paris and Glasgow Agreements have identified the reduction in carbon emissions as a prerequisite for preventing the potentially catastrophic repercussions of further global warming. In particular, the 2016 Paris Agreement was adopted by UNFCCC and has set the target to maintain the average temperature rise globally at no more than 2 °C in this century, and also to limit its rise to within a 1.5 °C increase compared to the same value at the pre-industrial era [41]. More recently, the Paris Agreement was updated and finalized in 2021 in the COP26 Conference in Glasgow, where all of the nearly 200 participating countries agreed to revisit and strengthen within 2022 their respective current emissions targets for the year 2030, the so-called “Nationally Determined Contributions (NDCs)”. Even more importantly, heeding calls from civil society and sovereign nations that are most susceptible to impacts from climate changes, the COP26 agreed for the first time on actions regarding the phasing *down* or even phasing *out* of fossil fuels [42]. To achieve these goals, the European Commission adopted at 2021 a series of proposals to render the EU’s climate, energy, transport and taxation policies suitable towards the goal of reducing greenhouse gas emissions by at

least 55% (compared to 1990) by 2030, the so-called “EU Green Deal”. Indeed, the achievement of such reductions in the next decade is crucial to Europe becoming the world’s first climate-neutral continent by 2050 and effectively materializing the European Green Deal [43]. Similarly, in the United Kingdom, the government has set a target of an 80% CO₂ emission reduction by 2050 [44] and India aims to reduce a third of its respective CO₂ emissions by 2030.

All the above climate goals represent the ambitious strategies for which most nations have agreed to mitigate climate change, amid multi-decade international debates and discussions, that it would avert a dangerous interference with the climate, ensuring at the same time sustainable economic development and food availability [40,45]. Limiting global warming to any level, even by less than 1 °C, implies that the total CO₂ amount that can ever be emitted in the air is finite. Geophysically, it is imperative that global CO₂ emissions reach net zero [45,46]. It is noteworthy that the IPCC’s Fifth Assessment Report indicated that about 2/3 of the available amount of CO₂ emissions (also called “CO₂ budget”) for maintaining a temperature rise below 2 °C had already been emitted as of 2016. In the same report, it is mentioned that the time window for a high-probability, below-1.5 °C scenario and the avoidance of even a temporary surpassing of this value seems to have been already closed [47]. Additionally, the worldwide increase in CO₂ emissions urgently indicates that this trend needs to be reversed, in order to hold the possibility of global warming to well below 2 °C [48,49].

Along with the mitigation of CO₂ emissions, another important step towards the aversion of catastrophic climate change is the profound transformation that the energy system globally must undergo, i.e., from a fossil fuel-based one to a renewable and efficient, as well as low-carbon (ideally zero-carbon) one [47]. According to a report by the International Renewable Energy Agency (IRENA), over 90% of the necessary global CO₂ emission reductions could potentially be achieved this way [17]. Additionally, renewable energy is widely expected to directly contribute by around 40% to the required CO₂ emission decrease and by an extra 13% via renewable electrification (indirect contribution) in the various consumption sectors, such as in transportation and industry. However, in order for this rather ambitious objective to be met, RES energy share in the global energy mix needs to increase from their 2017 value of 17% [50] and to account for roughly 2/3 of the final energy consumption by the year 2050. Variable renewable energy, in particular solar and wind, are projected to constitute the vast majority of the generation capacity and amount to ca. 60% of all electricity generation [17].

Nonetheless, these estimations could not, of course, take into account the profound changes brought in the energy sector by the global COVID-19 pandemic from 2020 onwards. Therefore, even though the effects of the global coronavirus crisis may not be fully unraveled as of yet, reports from the International Energy Agency and International Renewable Energy Agency with regard to the effect of COVID specifically in the renewable energy sector have already been published. These reports have concluded that the outbreak caused serious problems in the renewable energy sector, such as supply chain delays, difficulties in tax stock markets and inability and/or risk for the investors to benefit from government incentives and funds, which were allocated instead towards pandemic relief packages [51,52]. These facts have caused a postponement of many projects and an inevitable drop in the employment of RES energy projects and are further corroborated by several individual papers published after the coronavirus outbreak [53–56], highlighting the interconnectivity between various sectors and aspects in the modern, globalized economy. Another, equally important factor that inevitably needs to be accounted for with regard to energy transition is no other than the recent energy crisis further exacerbated by the Russian invasion of Ukraine in February of 2022. Similar to the COVID-19 pandemic, the toll that the ongoing tense situation in Ukraine will take on the energy sector worldwide in the coming months or years cannot be completely evaluated so far, as energy policymaking will be largely determined by geopolitical factors.

In any case, the Paris and Glasgow Agreements implicitly acknowledge these insights and aim to reach a peak in GHG emissions globally as soon as possible, along with achieving a balance between the penetration of variable RES, anthropogenic emissions and GHGs removal until 2050, even on top of the problems caused by the COVID-19 crisis.

4. CO₂ Mitigation Technologies

A sustainable energy policy in order to mitigate climate change and successfully address the Paris agreement directives is considered to be based on three pillars: (i) improvement of the efficiency of fossil fuel-based energy conversion, (ii) replacement of fossil fuels with energy sources that are more environmentally friendly and carbon neutral, such as renewables and (iii) capture, storage and utilization of unavoidable CO₂ emissions [57,58]. Amongst these, the second one, i.e., RES penetration in the energy mix is the most feasible from a practical point of view, albeit with the unavoidable requirement for governmental financial support (mainly via subsidizing). On the other hand, CCS and CCU technologies have recently gained great scientific interest as possible alternatives for reducing CO₂ emissions through its storage or valorization towards value-added chemical commodities and fuels [59], as discussed below.

4.1. Carbon Capture and Storage (CCS)

Carbon capture and storage (CCS) is considered to be one of the main pathways for reducing CO₂ emissions. The idea of CCS derives from the proposition that given the current inability to completely move away from fossil fuels (commonly referred to as phasing-out of fossil fuels), efforts should be made, at the very least, to capture the large amounts of CO₂ emitted from prominent fossil fuel consuming point sources such as power plants or industrial units, e.g., cement or iron/steel production factories. With CCS, CO₂ emissions are diverted from their release into the atmosphere via a dedicated capture technology, after which they can be separated from the associate mixtures, transported and then permanently stored, most commonly in deep formations underground and/or geological cavities that possess a very large capacity for carbon dioxide sequestration. CO₂ can also be stored in coal beds, oil wells and beneath the oceans, forming minerals and other inert carbonated compounds [60]. Notably, it is estimated that the potential supply of anthropogenically generated CO₂ is significantly larger than its demand, as globally around 500 Mtonnes of low-cost (less than 20 USD/tn) and high-concentration CO₂ streams are available as a by-product from natural gas processing, fertilizer plants or other industrial sources. Additionally, at a rather higher cost value (i.e., 50–100 USD/tn), around 18 billion tonnes could also be captured per annum from the dilute CO₂ streams currently emitted by power, steel and cement plants [8]. Transport of liquid or supercritical CO₂ is in theory feasible, given that conditions for this require a temperature of over 32 °C and a pressure higher than 73 atm [61,62]. The CCS approach can be thus considered as a medium-term solution and an intermediate step in the transition from the current energy systems to those that are characterized by carbon neutrality. The amount of scientific papers regarding CCS technology has largely increased in the past two decades, as the measures for CO₂ abatement have become increasingly stricter [59].

Another proposition is direct air capture (DAC), a concept first introduced by Lackner et al. in 1999 [63], and in which CO₂ is extracted directly from the ambient air. However, given the low concentrations of CO₂ in the air (less than 500 ppm), this technology has not yet reached the required maturity, although efforts are under way to improve and increase the associated technology readiness level (TRL) [64]. Detailed overviews of the current and future status of DAC can be found in [65–68]. In any case, CSS is so far largely associated with the capture of CO₂ from a stationary point source and this concept is schematically depicted in Figure 4 [69].

In light of the above, the European Union has adopted the Strategic Energy Technology (SET) for smart, adequate and sustainable growth, including energy and climate challenges [70]. The SET Plan considers that CCS technology plays a key role as an alternative in

CO₂ emission mitigation, although substantial efforts are required to overcome the barriers hindering its commercial implementation. These barriers include the energy-intensive character of this technology, low overall efficiency in power plants and/or industrial processes, high capital and operational expenditure, lack of Europe-based infrastructure for CO₂ transport, safety issues regarding long-term CO₂ storage, social acceptance, CO₂ tariff and lastly regulatory framework [71].

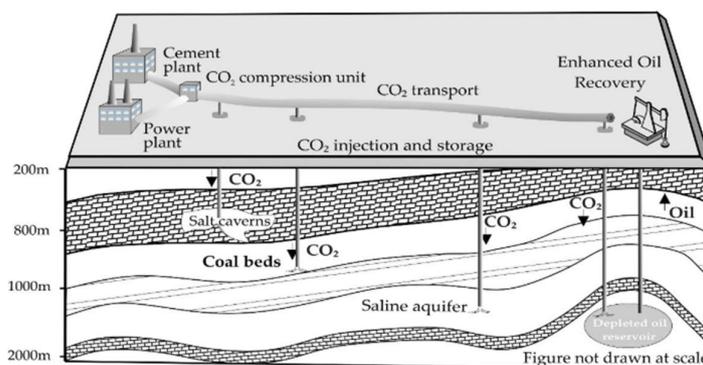


Figure 4. Basic principle of Carbon Capture and Storage from a stationary point source. Reprinted from [72].

Given the above, it becomes evident that the main interest in CCS project implementation comes from large CO₂-emitting sources. As mentioned earlier and according to 2018 data from the IEA, the main carbon-emitting industry sectors are cement, iron/steel and chemical/petrochemicals, as shown in Figure 5. Therefore, the integration of a suitable CCS technology with the concentrated amount of CO₂ that is present in the effluent streams of these plants may be an effective way to reduce their carbon footprint. Other pathways attracting a lower (but not insignificant) amount of scientific interest for CO₂ capture concern the use of algae [73,74], biochar [75,76], nanomaterials [77,78] and charcoal [79]. Detailed information about the current state of CCS plants worldwide can be found in the latest report of the Global CCS Institute [80], an international think tank whose mission is “to accelerate the deployment of carbon capture and storage”. According to the Global CCS Institute’s CO2RE database [81], as of 2018, there were 23 large-scale CCS facilities in operation or under construction, with an annual CO₂ capture capacity of almost 40 Mt. Added to this, 28 pilot and demonstration-scale facilities are in operation or under construction. Collectively, these plants are able to capture more than 3 Mt of CO₂ per annum [80].

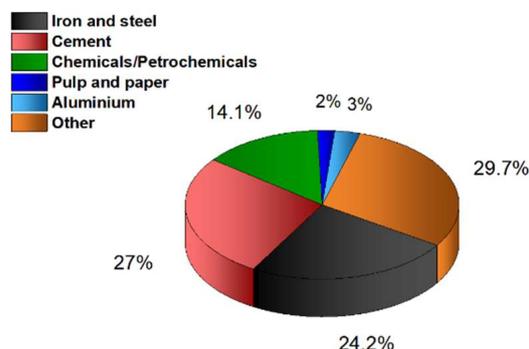


Figure 5. Industry sector-divided direct CO₂ emissions in 2018. Created by the authors using data from the International Energy Agency [2].

Elaborating the above, there are three general approaches for the capture of CO₂ from a power plant, with regard to the stage in which the capture is taking place: pre-combustion, oxy-fuel and post-combustion [82–84]. The general principles of each method are illustrated in Figure 6, followed by a brief description.

- **Pre-combustion** or fuel decarbonization is associated with the removal of carbon from the fuel and the eventual combustion of its hydrogen content in an energy conversion device. At this stage, a carbon-containing solid fuel is decarbonized before its utilization in a gaseous stream via a gasifier and a catalytic reactor. Firstly, syngas (a gas mixture containing predominantly CO, H₂ and CO₂) is formed in the gasifier under sub-stoichiometric oxygen conditions. Secondly, syngas reacts with steam in the shift reactor for its enrichment in CO₂ via the water-gas shift reaction. Instead of solid fuels, natural gas can also be used for pre-combustion capture via the reaction of steam reforming, which also yields syngas [85]. The captured CO₂ in the effluent can be compressed, dried and separated by the commercially available technique of physical adsorption. A summary of some important studies on pre-combustion processes is included in [86].
- **Oxy-fuel combustion** involves the burning of the fuel (mainly coal) in the presence of pure oxygen instead of air, thus eliminating nitrogen dilution of flue gases. The N₂-free and O₂-rich reaction atmosphere minimizes CO formation and results in a more concentrated CO₂ stream in the final flue gases, largely reducing its purification demands [76]. CO₂ capture may then take place from flue gases by water condensation accompanied by compression and appropriate storage. This method was developed in the 1980s for the generation of high-purity CO₂ for enhanced oil recovery. The required oxygen during the initial stage is provided by means of a cryogenic distillation unit and appropriate conditions are maintained by mixing the flue gases with pure O₂ before combustion [87]. Oxy-fuel combustion is potentially highly advantageous in terms of feasibility, albeit the high requirements of pure oxygen inevitably increase the overall cost. However, together with pre-combustion capture, these approaches are adaptable to transportation applications [88].
- **Post-combustion carbon capture (PCC)**. As the name suggests, CO₂ in PCC is captured in the stage following combustion, i.e., from a CO₂-rich exhaust gas. PCC is currently the most accessible option among all capture technologies, as it is an established process and currently in use in various industrial applications [89–91]. In fact, the proposal of PCC started in the 1970s as a potentially economical source of CO₂, mainly for enhanced oil recovery (EOR) operations. Therefore, PCC differs from pre-combustion and oxyfuel methods, in the sense that the latter two are still in their developmental phase. PCC is also now the most accessible option for retrofitting already existing plants and lowering their carbon footprint, though this is not always applicable in a cost-effective way [92]. A few technologies have been proposed as alternative approaches for PCC and a comprehensive review by Mondal et al. provides detailed information about these approaches [93].

However, in spite of its attractive potential as a global warming mitigation option, there are several uncertainties with regard to CCS development, specifically life-cycle effects, costs, storage permanence, potential back-leakage of CO₂ into the atmosphere and overall capacity [94]. Furthermore, inefficient framework and power penalties pose further significant considerations for the full-scale implementation. Primarily, CCS involves processes that are energy-intensive and currently associated with high operational costs, such as the technique of carbon capture itself, power generation and maintenance of the overall process. Additionally, as is always the case, the average storage cost mainly depends on the extent of the network as well as facilities location. For the proper implementation of CCS, adequate global policies and regulations and intergovernmental cooperation are required to address the lack of incentives and capital availability. The collaboration between CCS storage and emission source operators can achieve productive enforcement of CCS technology [82,85].

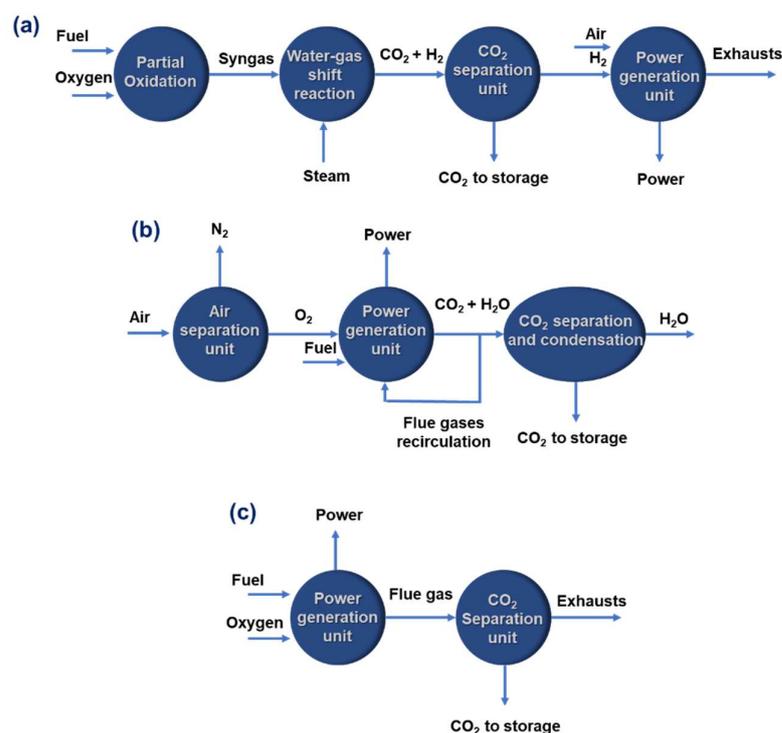


Figure 6. Basic principle of CCS in a power plant during pre-combustion (a), oxy-fuel combustion (b) and post-combustion (c) Adapted from [93].

Regarding further reading, there are several review papers in the scientific literature addressing the recent progress in CCS. In particular, modeling of CO_2 capture via chemical absorption has been studied extensively and the most recent advances have been reviewed extensively [7,86,95–98], whereas a study of pilot-scale projects was conducted by Yan and Zhang [4]. Budzianowski [97] reviewed the mechanisms of different solvents applied in chemical absorption of CO_2 . Moreover, an assessment of the main barriers for PCC schemes was also proposed with the evaluation of several process intensification technologies [5,99]. A particular focus on CCS technologies in a specific process is also available for refineries [100], power plants [83,86,98,101], the cement industry [64,102–104] and for comparative assessments for various carbon-intensive industrial processes [5,31,105,106]. In terms of environmental impact of CCS schemes, the work by Volkart et al. [107] provided a life cycle assessment (LCA) of carbon capture and storage in industry and power generation in Europe.

4.2. Carbon Capture and Utilization (CCU)

An option that is potentially more attractive than CCS since it can act as complementary to it, is Carbon Capture and Utilization (CCU). CCU techniques are generally classified into two categories, i.e., direct use and conversion of CO_2 . In both cases, in CCU the captured CO_2 is not directed to a permanent storage location but is instead used either directly or indirectly via its conversion. According to the Global CCS Institute, there are already many existing industrial uses for carbon dioxide, with the current global “non-captive” consumption estimated to be approximately 80 Mtonnes annually, comprising of 25 Mtonnes in the liquid and solid form and the remainder in gaseous and supercritical form. Direct uses of CO_2 primarily refer to uses in the enhanced oil and enhanced gas recovery (EGR) as well as enhanced geothermal systems (EGS) in large-scale industries (Figure 7) [108–110]. Specifically, enhanced oil recovery accounts for approximately 50 Mtonnes of CO_2 annually, 4/5 of which is supplied from natural CO_2 reservoirs at a price between 15–19 USD/tonne [8]. Additionally, it can be used as a useful compound in non-chemically oriented uses via its physical utilization as dry ice, fire extinguisher,

solvent, carbonating medium in beverages, process fluid and welding medium. Since the direct (physical) use of CO₂ is beyond the scope of the present article, its chemical use as a reactant will be discussed in more detail.

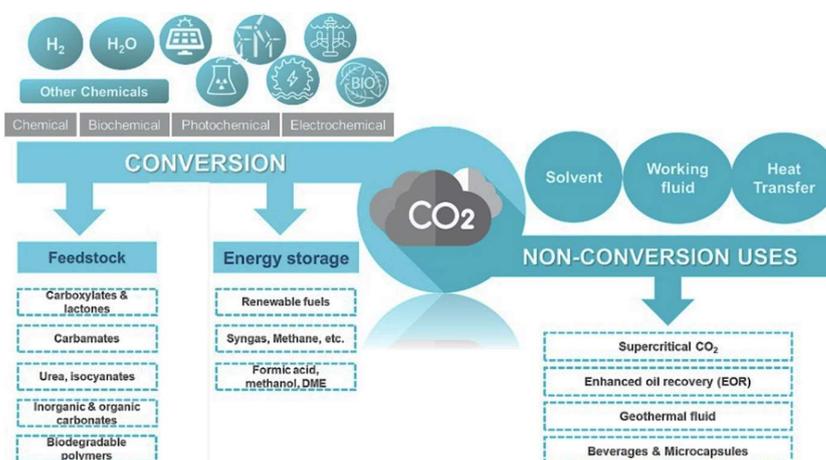
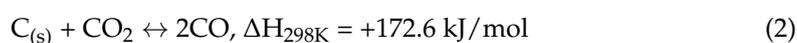
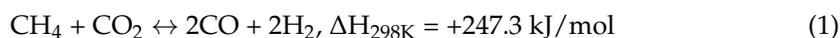


Figure 7. Different pathways for utilizing carbon dioxide. Adapted from [111].

In essence, CO₂ conversion describes its transformation into different compounds containing the carbon from the parent molecule of carbon dioxide. Recent advances in industrially used CO₂ showcase that each conversion pathway is inevitably associated with certain benefits and drawbacks [31,112,113]. Indeed, they can potentially lead to a plethora of products intended for the chemical and energy sectors and include organic synthesis or electro-reduction (CO₂ electrolysis), mineral carbonation or hydrogenation. In general, the main CO₂ utilization routes are commonly classified into three groups: chemical conversion, mineralization and bio-based routes.

Currently, only a small percentage of globally available CO₂ is used directly in the chemical industry as feedstock. The predominant chemical utilization pathway is that of urea production with NH₃ at temperatures and pressures higher than 180 °C and 150 bar, respectively [114]. Other uses of CO₂ in the chemical industry are its involvement in dry reforming of methane (DRM) for synthesis gas production via a strongly endothermic process (Equation (1)) or carbon gasification (of the reactive carbonaceous content in either coal, lignite, biomass, waste, etc.) via the reverse Boudouard reaction for the production of CO (Equation (2)). A comprehensive summary of the technological and economic prospects of various CO₂ utilization pathways is described in the work by Hepburn et al., [115].



Moreover, one of the most successful processes for CO₂ utilization for organic material synthesis is its catalytic conversion into fine chemicals such as cyclic carbonates and polycarbonates from high-energy epoxide compounds, a process that can already be industrialized [116]. Other commercially implemented uses include using CO₂ as an additive to CO for methanol production [117], polycarbonate polyols manufacturing [118], dimethyl carbonate production [119] and more. The aforementioned routes involve the thermochemical conversion of carbon dioxide. However, other two established pathways have begun to attract scientific interest, namely electroreduction and photocatalytic reduction of CO₂. The former also includes the innovative scheme of co-electrolysis of CO₂ and H₂O for syngas or other added-value chemicals production [120–122]. Details about these technologies is beyond the scope of this review and the reader should refer to the respective literature for electrocatalysis [123–126] and photocatalysis [127–129] of CO₂. Lastly, a large family of value-added chemicals can be produced by the process of direct CO₂ hydrogenation, which is discussed in more detail in the next section.

Collectively and in accordance with the Paris Agreement directives, there has been a worldwide effort towards the goal of CO₂ emissions abatement worldwide. Indeed, although not all of the proposed technologies for carbon dioxide mitigation are necessarily Paris-compatible and economically feasible in the long term [58], increased funding has been allocated for the deployment of several projects globally [4,130–132]. In particular, in 2020, the USA government approved the US Energy Act, authorizing the allocation of ca. USD 6 bn for CCS research, development and demonstration, while CCS project developments in Canada were greatly accelerated with newly proposed incentive policies and continued investments. Elsewhere, the Australian government has included CCS in the Emissions Reduction Fund, providing the first financial incentive scheme for CCS in the Asia-Pacific region. Additionally, the first commercial CCS projects were announced in Malaysia and Indonesia, while China has pledged to achieve its carbon peak prior to 2030 and carbon neutrality before the year 2060. The latter has raised the relevance of subsequent CCS project development milestones at a national level. As for Europe, there are now 35 CCU projects in development, while the UK alone announced a 1 billion GBP CCUS infrastructure government fund, outlining its intention to establish four CCUS industrial clusters by 2030, capturing 10 Mtpa of CO₂. Additionally, given their prominent role in oil production capacity globally, the Gulf Cooperating Council (GCC) member states already account for 1/10 of the total amount of captured CO₂ annually, poised for a significant take-off in CCS activity over the next decades, with projections for a CO₂ capture capacity as high as 60 Mtpa by 2035 in the GCC region. In all, these efforts have led to the development of a total of 134 commercial facilities in operation and/or under construction worldwide, with an estimated total capacity of around 37 Mtonnes of CO₂ per year, the majority of which located in the United States. In any case, even more detailed information as well as further regional breakdown of the various CCS and CCU projects on a global scale can be found in [4,130–132] and references therein.

Lastly, although there are several proposed technologies for the effective mitigation of CO₂ emissions, it is inevitable that the selection of an appropriate method for the implementation of a large-scale relevant CCS and/or CCU project will be determined by the cost-effectiveness of each particular method. Additionally, it becomes apparent that the feasibility of a CCU project is case-specific and it is largely determined by the respective downstream process after CO₂ capture itself, rendering the direct comparison of CCU costs practically irrelevant. However, the same does not apply to CCS schemes, since they are associated with lower complexity and are basically dependent on the method applied for the capture of CO₂ (i.e., the final product is always a stream of CO₂). In this regard, a cost comparison of the various technologies according to the literature is summarized in Table 4. Evidently, the capture of CO₂ directly from atmospheric air is by far the most expensive process, mainly ascribed to the very low carbon dioxide concentrations in the air. At the same time, the most efficient technology is pre-combustion of coal or natural gas, as it is associated with a high CO₂ concentration, which favors the adsorption efficiency. Thus, it is a fully developed technology that is commercially deployed at industrial scale [132,133]. Additionally, although removal efficiency values are in general relatively high (i.e., more than 80%), in the case of CO₂ capture from power plant flue gases, they need to be amped up even further in order to improve the cost-effectiveness of the employed CCS/CCUS technology, since the eventual electricity cost can be increased up to 90% [134].

However, it should be noted that given the inherent uncertainties that are present in every economic analysis, as well as the variabilities in the corresponding Technology Readiness Level (TRL) and the unpredictability of future projections due to learning curves and economies of scale, these values are no more than an estimation and they need to be evaluated and updated constantly and on a case-specific basis. What is more, as already stated for RES energy development (see above), the status of CCS/CCU projects also needs to be contextualized in terms of the post-COVID era. In this sense, it is generally believed that even though the coronavirus crisis largely shook the world and especially the energy sector by means of unprecedented reductions in energy demand and CO₂ emissions

directly attributable to lockdown measures, the long-term picture for CCS/CCU has not changed [131]. Nevertheless, the direct effect of COVID-19 pandemic in the CCS/CCU industry cannot be thoroughly evaluated as soon as now, thus it needs to be monitored in conjunction with the pandemic-induced fluctuations in the energy sector. In any case and along with the COP26 conclusions, there is a unique opportunity to bring climate change mitigation efforts to the forefront of investment policies and scale up funding for climate action, including CCS/CCU.

Table 4. Cost comparison table of various CO₂ mitigation technologies.

Technology	CO ₂ Removal Efficiency (% v/v)	CO ₂ Capture Cost (EUR/tn)
Industrial separation	90	32.9–57.3
Pre-combustion	88	31.9–59.1
Oxy-fuel combustion	>90	48.9–55.7
Post-combustion	90	43.2–69.5
Chemical looping	96–99	<56.0
Direct air capture	85–93	131.4–319.1

Created by the authors using data from [132].

5. Valorization of CO₂ Emissions via Hydrogenation

5.1. Fundamentals of CO₂ Conversion Using H₂

As is the case for every chemical reaction, the CO₂ hydrogenation reaction is inherently driven by differences in the chemical potential between the reactants and products under given conditions, as shown by the fundamental Gibbs–Helmholtz relationship between Gibbs free energy, enthalpy and entropy; $\Delta G^0 = \Delta H^0 - T\Delta S^0$. Both ΔH^0 and $T\Delta S^0$ are usually not favorable in the conversion of carbon dioxide. Given its very low Gibbs energy ($G_{298K} = -393$ kJ/mol, see Figure 8), CO₂ as a compound is very stable thermodynamically, with carbon being present in the maximum oxidation state of +4 by forming two double bonds with oxygen, which are characterized by excessive strength and overall stability. This is demonstrated by the very high dissociation energy (750 kJ/mol) for each C=O bond, higher than the respective values for C-C (336 kJ/mol), C-O (327 kJ/mol) or C-H (441 kJ/mol) bonds [135]. Thus, any attempt to use CO₂ as a reactant must take into consideration the stability of the reaction products compared to the reactants, as well as the intrinsic barrier of the cleavage of the two strong C=O bonds. Another issue that needs to be accounted for is that many of the final CO₂-derived products are liquids (e.g., methanol, formic acid, higher hydrocarbons), thus their respective formation reactions are disfavored entropically.

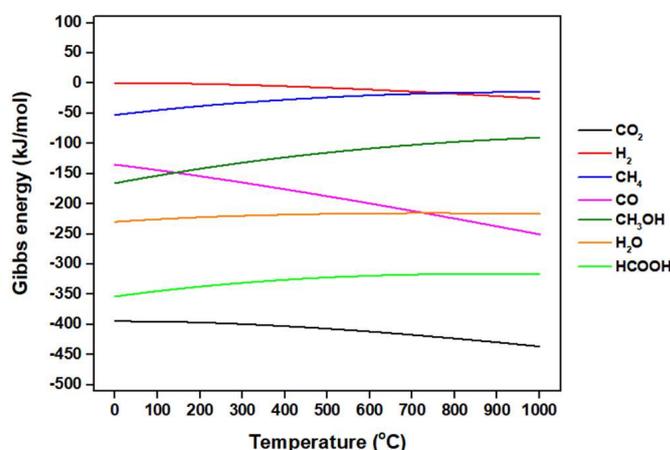


Figure 8. Gibbs free energy values of pure components at 1 bar as a function of temperature.

In general, CO₂ conversion processes can be divided in two categories [136]. The first category involves reactions where the second reactant (aside from CO₂) is characterized by higher Gibbs free energy and the entire molecule of CO₂ is inserted onto an organic substrate, such as the production of carboxylates, carbamates, lactones, carbonates and isocyanates. These processes are energetically favorable and do not necessitate the use of a catalyst, since the oxidation number of C is maintained at +4. Additionally, reactions of the first category typically take place at the low-temperature regime, between −30 to 150 °C. The second category includes carbon-reducing reactions, with the concomitant requirement of a substantial amount of external energy, typically occurring at higher temperatures, ca. 300–600 °C (Figure 9) [137]. Examples of the latter category include CO₂ reduction into formates, oxalates, CO, CH₃OH or CH₄. The external energy is generally provided thermally (i.e., by heat), though the use of a catalyst substantially enhances the reaction kinetics by providing a pathway with a decreased activation energy. An extensive overview of the catalytic materials used in CO₂ hydrogenation can be found in a plethora of recent literature reviews [137–143].

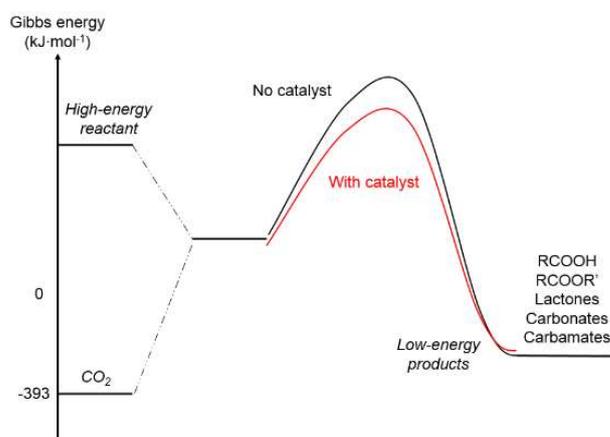


Figure 9. Energy levels of carbon dioxide, high-energy reactants and low-energy products. Adapted from [144].

In this sense, the catalytic reduction in carbon dioxide via its reaction with the energetically dense and high-Gibbs energy molecule of H₂ has been widely proposed to be an effective way to transform the inert molecule of CO₂ to a variety of products. Indeed, hydrogen can initially provide a significant energy load that, along with another form of energy, most commonly heat, can induce molecular bond-breaking and generate a plethora of organic compounds. Product distribution during CO₂ hydrogenation varies widely and depends on many parameters such as pressure, temperature, H₂:CO₂ ratio, presence of CO, H₂O and/or CH₄ in the reactant feed, nature of catalyst, contact time and more.

The possible products that can be formed by this process are not limited in the C₁ group, but include many C₂₊ ones such as dimethyl ether (DME), higher hydrocarbons and higher alcohols (Figure 10). Each one of these products can be used in a variety of processes, either as fuel (in the case of CH₄, CH₃OH, CH₃CH₂OH, DME and hydrocarbons) or as valuable chemicals (such as formaldehyde, dimethyl carbonate, light olefins, amines and aromatics). Thermodynamically, methane is by far the most favorable C₁ product, as seen in Figure 11a,b. It should be stated that given that the production of CO via the reverse water-gas shift (rWGS) reaction is not associated with a change in the number of moles in the gas phase, the effect of pressure is expected to be practically negligible.

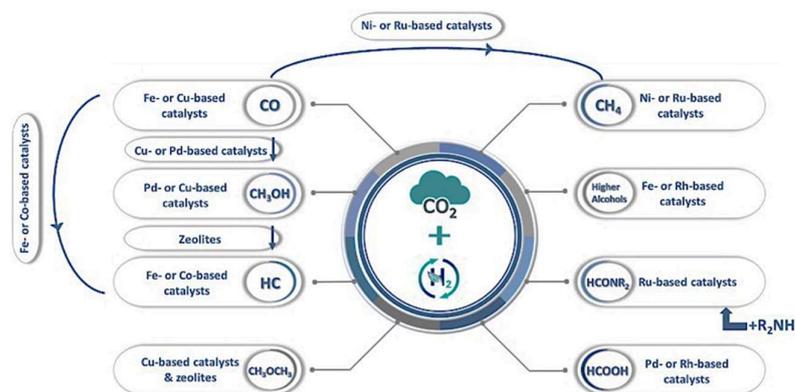


Figure 10. Possible CO₂ hydrogenation products. Adapted from [145].

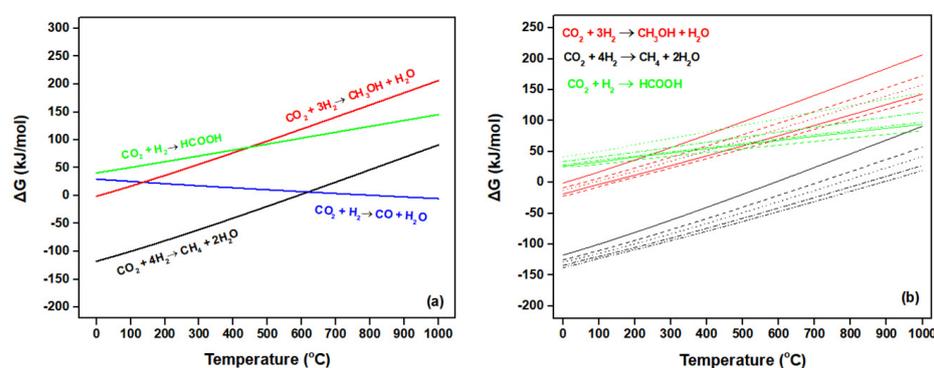


Figure 11. Gibbs energy change for CO₂ hydrogenation to C₁ products at 1 bar (a) and effect of pressure (b). Solid line: 1 bar, dash: 5 bar, dot: 10 bar, dash dot: 20 bar, dash dot-dot: 30 bar.

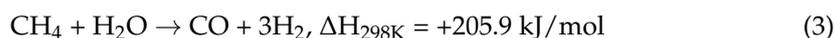
5.2. Sustainable H₂ Production via Renewable Energy

In order to design a general process that mitigates CO₂ via its hydrogenation to value-added products, one needs to take into account that hydrogen is not an abundant standalone source and therefore needs to be generated/extracted from water or/and hydrocarbons at relatively large-scale capacities. Even if the capture of CO₂ from the flue gases of a power plant and its transport to the hydrogenation facility is successfully realized, the added value of the possible products and the overall carbon footprint and environmental impact of the scheme will be more or less dependent on the employed energy source and selected route to produce hydrogen.

Therefore, in order for hydrogen to fulfill its future potential as a key energy currency in a decarbonized and hydrogen-based economy, its mass production must proceed in a sustainable way, a prerequisite of which is that clean hydrogen becomes cost-competitive with conventional fuels, estimated at a final production cost between 1.5–3 EUR/kg H₂ [146]. These production costs are viable for both conventional steam methane reforming (SMR) with CCS and for the electrolysis of water. For example, fuel cell cars are projected to achieve similar costs with diesel ones in commercial-scale production capacities, at a cost of 5 EUR/kg H₂, whereas industry and gas-clean hydrogen may reach parity with fossil-based inputs after including the carbon cost [147]. Recently, a consortium of international corporations formed the Hydrogen Council, as a means of placing H₂ among the key solutions in the general scheme of energy transition and have provided a 2050 roadmap based on a hydrogen-based economy [18].

Comprehensive technological overviews of methods for hydrogen production, along with a discussion about major challenges, R&D priorities and potential prospects of H₂ can be found in recent reviews [148,149]. In general, there are three main routes for industrial-scale H₂ production and these are aptly referred to as grey, blue or green hydrogen production schemes, denoting the overall environmental footprint of the respective

generation scheme [150,151]. This is better visualized in Figure 12, which also shows the desired shift towards sustainability. However, the process of the so-called “grey hydrogen” production via the reforming of predominantly natural gas (mostly referred to as steam methane reforming, SMR) or other fossil fuels, such as liquified petroleum gas (LPG) or gasoline, dominates global production (over 95%), reaching approximately 100 Mt per year [152,153]. This is achieved in a reformer reactor, in which water vapor under high temperature and medium pressure (between 700–1100 °C and 5–25 bar, respectively) reacts endothermically with methane, (Equation (3)) in the presence of a suitable catalyst [154,155].



However, SMR produces a hydrogen mixture with relatively low purity, containing appreciable amounts of carbon oxides, CO_x . Two more environmentally sustainable alternatives to the conventional SMR process exist, however. These refer to either SMR integration with a CO_2 capture and storage unit or the implementation of large-scale biomass gasification and methane decomposition (or pyrolysis) processes, collectively known as “blue hydrogen” technologies.

In light of the above, increased scientific interest has been attracted over the past decades to boost the production of the so-called “green hydrogen”, i.e., H_2 produced by a process with a near-zero carbon print, though it has to be mentioned that there are no globally agreed and/or standardized definition of green H_2 as of yet. Possible pathways for green H_2 production involve the reforming of liquid/gaseous biofuels, thermochemical water splitting, photocatalysis, and combined anaerobic digestion and dark fermentation. However, the technological maturity of the aforementioned processes is still relatively low compared to SMR technology and their economic viability is questionable [17,152].

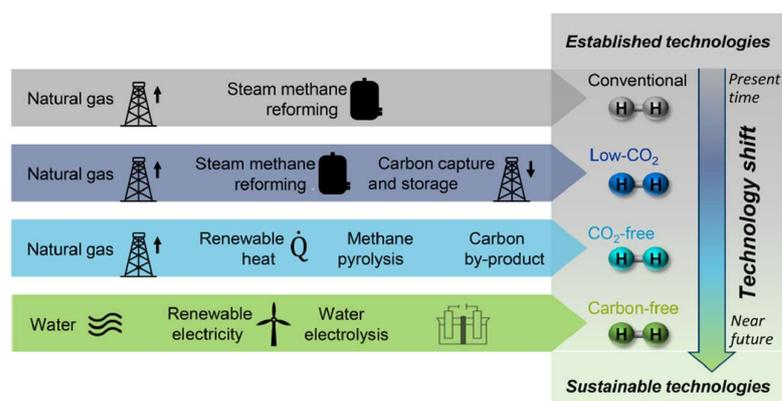


Figure 12. Visualization of the main routes for H_2 generation. Reprinted with permission from [151].

The most promising scheme for green hydrogen production, however, is no other than the use of the excess energy produced by renewable energy sources to electrochemically split water into its constituents. In this way, excess power generated in times of reduced electricity demand (and/or increased energy supply) can be converted into a stable form of chemical energy, either directly through H_2 production or indirectly through the formation of CO_2 hydrogenation products in downstream catalytic processes. Even more importantly, one must take into consideration that a major issue regarding the large-scale penetration of renewables in the global energy mix is the fact that renewable energy generation via photovoltaic systems or wind generators is inherently intermittent owing to inevitable fluctuations due to the dynamic natural conditions [156]. Therefore, in times of surplus renewable power, energy storage technologies should be adopted to tackle with the mismatch of electricity supply and demand and provide grid stability and flexibility [14,157]. To this direction, the direct conversion of excess renewable energy into hydrogen can offer a sustainable approach to store large amounts of energy over long periods in the form of

chemical energy, facilitating the stability of the electricity grid as well as the large scale integration of unstable renewables to various applications and sectors [158].

In particular, the exploitation of a variable renewable energy source such as solar or wind for water electrolysis is gaining advantage as the most promising technology for green hydrogen generation, though efforts still need to be made to increase the efficiency and scalability of the technology as well as to substantially decrease the capital and operational costs [159–162]. In essence, the overall reaction of electro-chemical water splitting is the following (Equation (4)):



Stoichiometrically, the volumetric (or molar) production of hydrogen is two times the co-production of oxygen, with both gases produced at different compartments with a purity of more than 99.9% or even higher after final purification steps, depending on their final use. Oxygen can be simply vented out or be preferably exploited as a market product for use in the chemical or the metallurgical industry or even for medical use, although its utilization strongly depends on local market conditions, mainly the level of consumer's demand and the distance to potential customers [163].

The overall energy demand is given by the reaction enthalpy change, $\Delta H = \Delta Q + \Delta G$. From this equation, it is derived that the required energy can be only partly supplied by heat (the term ΔQ), whereas the term of the Gibbs energy change, ΔG , has to be supplied by electric energy. Additionally, ΔH varies only slightly with temperature (283.5–291.6 kJ/mol H_2 between the wide range of 0–1000 °C). However, the possibility of heat integration, ΔQ , increases with temperature, thereby reducing the minimum electrical demand expressed by ΔG [164]. Aside from the enhancement of the reaction kinetics, the possible exploitation of the high heat stemming from internal losses is a rather major incentive for operating the process at elevated temperatures (700–900 °C). Additionally, the heat demand corresponding to the water latent vaporization heat is partially supplied by feeding gaseous and not liquid water, as in low-temperature electrolysis technologies.

Advancing from the fundamentals of H_2O electrolysis, there are now several technologies, both on a lab and an industrial scale. The main difference between them is the type of the employed electrolyte which separates the two half-cell reactions at the anode (oxygen evolution reaction, OER) and cathode (hydrogen evolution reaction, HER) of the electrolyzer and thus the configuration of the particular systems. Technical differences between the different technologies include the operating temperature, operating current density and cell voltage, class of electro-catalytic and electrode materials and pH value. The major types of electrolyzers that are commercially available are; (i) alkaline electrolyzers (AEL), (ii) proton exchange membrane electrolyzers (PEMEL) and (iii) solid oxide electrolysis cells (SOEC). The former two types and especially AEL have achieved commercialization and typically operate in near-ambient temperature (usually up to 90 °C), whereas SOEC are characterized by a low TRL and they operate at significantly higher temperatures, typically between 700 and 950 °C [164,165]. The interested reader can find detailed information of each technology regarding operation, state-of-the-art and future implementation projects in dedicated reviews in the literature [16,153,159,161,164–166].

6. The Scheme of CO_2 Hydrogenation

6.1. Integration of Captured CO_2 with RES-Derived H_2

As mentioned so far, it is expected that in the near future large quantities of rather pure CO_2 will become available, since carbon capture from several point sources is becoming more or less a necessity, given that a complete and rapid decarbonization at a global scale is still infeasible or even practically impossible. However, given the uncertainties and the inherently slow process of natural recycling of sequestered carbon underground, it can be reasoned that direct utilization of CO_2 instead of its storage is the most efficient way of closing the human-induced carbon cycle in time frames that are meaningful for (and can be monitored by) humans. On the other hand, it is also expected that even larger supplies of surplus electricity will be generated in the future, due to the increased share of variable

renewable sources in the energy mix in most parts of the world, leading to increased need for RES energy curtailment [148,167]. Nevertheless, given the bottlenecks in large-scale electricity storage and the absence of other available transformation technologies at a sufficiently high TRL, this unavoidably intermittent excess electric energy is essentially projected to drive the development of readily available and mass-produced H₂ via water electrolysis [19,148].

Even though the utilization of H₂ and/or storage of CO₂ are being considered and are being widely studied as individual schemes per se, several benefits can also arise from the integration of these two abundant-to-be sources in the route of CO₂ hydrogenation. Indeed, in realistic projected scenarios where CO₂ storage and standalone H₂ utilization are materialized to a certain extent, the complementary implementation of CO₂ hydrogenation projects can provide substantial versatility to the various systems and sectors, as will be required in the increasingly advanced societies of the future. This is based on the fact that the combined catalytic conversion of hydrogen and carbon dioxide is a process that can be realized via many different sources of energy and is not limited to the conventional thermal route [113]. Namely, the overall scheme of CO₂ hydrogenation can proceed by the provision of alternative forms of energy, i.e., light [28,168–170], plasma [171–173] and electricity [125,174,175] as well as in the gas, solid and liquid phase either homogeneously [176–178] or heterogeneously [114,136,137,145,179,180]. Even more importantly, most of the aforementioned pathways are not limited to the production of a single product, but can potentially be fine-tuned for the selective production of a whole network of different products under variable reaction conditions and catalytic materials. Ergo, it can be reasonably postulated that once the availability of the reactants is established, the process of CO₂ hydrogenation can be potentially applied to a diversified pool of process operating conditions and for the satisfaction of a case-specific end product [178].

In addition, further integration of CCU with RES-powered water electrolysis in a power plant or a cement or iron/steel industrial unit can be made by the exploitation of not only hydrogen, but also oxygen that is also produced in the electrolyzer. Indeed, both electrolysis products can be potentially utilized in a closed loop where the pure oxygen stream is not vented out or sold but is used directly in an oxygen (or oxygen-enriched) burner for electricity generation or heat production via oxy-fuel combustion (vide supra). The selected fuel can essentially be a stream of synthetic natural gas produced catalytically on-site by H₂ provided from the electrolysis and the post-combustion CO₂ that is available after condensation of water and purification [181–183] or even solid biomass [184,185]. Additionally, since H₂O is a major product in any CO₂ hydrogenation reaction and provided that CO₂ is properly purified before entering the reactor, the collected water can be considered as a direct input to the electrolyzers without the need for pretreatment, further highlighting the cyclic character of the process [185,186].

Furthermore, even though the direct use of electrolytic hydrogen and carbon dioxide (e.g., fuel cells or as feedstock in “green” ammonia synthesis and geological storage, respectively) can potentially be advantageous in the long term, they are not yet optimized, are not available at large scales and can be hindered by several unforeseen socio-economic barriers [94,187,188]. Additionally, one could argue that in the case of CO₂ hydrogenation, the presence of an additional process step (i.e., the reaction/purification unit) prior to the final product adds more complexity compared to the direct use of H₂. Nevertheless, almost all of the many different products that can be derived from CO₂ hydrogenation (Figure 10) can be used in sectors that are widely established, almost fully optimized and associated with an already large product capacity, most prominently the natural gas grid or the methanol industry. Moreover, the added-value of the generated products through the hydrogenation of CO₂ can be potentially significantly higher than the one for H₂, in the case of C₁ products [189,190] but more importantly for C₂₊ compounds such as dimethyl ether, C₂–C₄ olefins, light hydrocarbons, etc. [112,180,191,192].

6.2. Power-to-X Processes

In light of the above, it has been established that a stream of CO₂ captured in the effluent gas of a CO₂-emitting industrial process can be coupled with a stream of green H₂ from RES-powered H₂O electrolysis process to ultimately transform excess energy and at the same time mitigate CO₂ emissions towards value-added organic chemicals or synthetic fuels. The as-proposed overall scheme can theoretically provide a carbon-neutral circular scheme, through which any CO₂ emitted by the end product can be re-converted into some form of green energy and is generally labelled as “Power-to-X” or “PtX”, where “X” stands for the various end products. Collectively, the various routes are illustrated in Figure 13, while evaluations regarding the use of different CO₂ sources for PtX processes can be found elsewhere in the literature [84,193,194]. Provided that the stages of CO₂ capture and electrolytic H₂ production are installed and operating harmoniously, Power-to-X can be adapted for different geographic locations and/or supply/demand variations, so as to effectively make use of the reactant mixture of CO₂ and H₂. A specific Power-to-X conversion route may thus be selected based on demand for a specific product (that is, the X in PtX), technical characteristics, environmental impact and levelized cost, in direct comparison with the available alternative solutions.

Finally, another critical advantage for the development of a PtX process based on CO₂ hydrogenation is the inherent issues associated with managing hydrogen as a standalone gas. On the one hand, hydrogen is highly flammable, so storage in its gaseous form is a challenge due to safety reasons arising from leakages, especially in densely populated areas [188,195]. On the other hand, although hydrogen storage has been implemented in the industry for several years, the scaling up of storage capacity and the readiness with which it can be resupplied on a short-term basis to the existing energy system (taking into account the intermittent nature of its RES-powered production), along with environmental issues, requires further research [147]. However, multiple considerations need to be taken into account for the feasibility assessment of implementing PtX at industrial scales, both from a techno-economical and an environmental point of view.

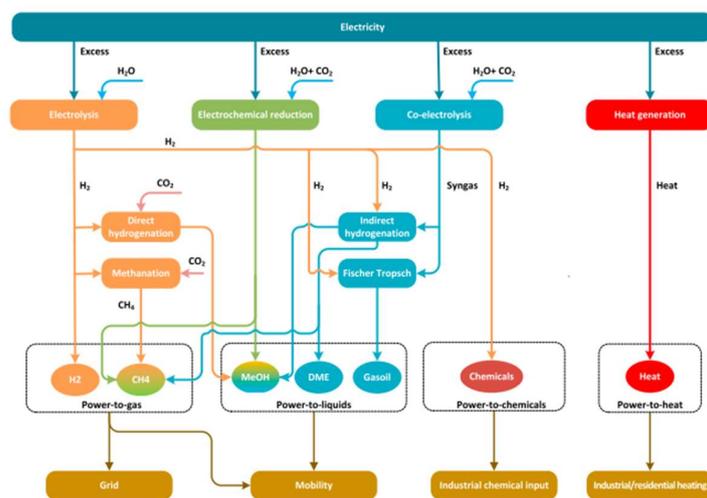


Figure 13. Schematic representation of the various Power-to-X routes. Reprinted from [196].

In the following, the most commonly considered processes under the general term “Power-to-X” are shortly described;

- **Power-to-Heat (PtH):** A coupling of the heat and power sectors appears to be a rather promising strategy for addressing energy decarbonization and RES-energy intermittency. To this end, several PtH technologies that can potentially contribute to decarbonizing heat supply along with integrating the variable renewable electricity, if sufficiently flexible, are available. In the scheme of PtH, typically, electric boilers, heat pumps or furnaces are used to convert RES energy to heat [197], which may be a sig-

nificant product in regions with heat district networks (operating traditionally via the waste heat of coal power plants) [198,199] or for industrial facilities producing steam.

- **Power-to-Liquids (PtL) or Power-to-Chemicals (PtC):** The processes of PtL or PtC are associated with either electrolysis of H₂O for H₂ production and subsequent hydrogenation of captured CO₂ emissions or the co-electrolysis of CO₂ and water for the production of liquid hydrocarbons via the Fischer–Tropsch synthesis or the methanol-mediated route towards specific fuels or chemicals. The produced fuels via the Power-to-Liquids process have the advantage of higher energy density products both in terms of volume and weight, rendering them ideal carbon-neutral substitutes for hard-to-abate sectors such as shipping, aviation, or heavy-duty trucks and lorries [200]. Moreover, many PtL products are considered value-added products which are conventionally produced from natural gas or coal. Notably, multi-source and multi-purpose alcohols are excellent candidate fuels, and CH₃OH and CH₃CH₂OH are actionable first targets with a potential of Gtonne-scale production [117].

Additionally, the storage of captured CO₂ and renewable energy in chemical energy is, in principle, preferable in oxygenated organic compounds such as alcohols or formic acid rather than in hydrocarbons, due to the lower requirements of hydrogen for their synthesis. Ergo, methanol, ethanol (obtained either directly or via the homologation of methanol) or even HCOOH are potential chemicals for long-term chemical energy storage and time-shifted power delivery, given the alternative of their use as liquid hydrogen carriers in fuel cells operating at high temperatures [201]. Consequently, PtL or PtC can lead to a coupling of the electricity and transport sectors (e.g., CH₃OH, DME) and the chemical industry (e.g., HCOOH, dimethyl carbonate, light olefins) [202].

- **Power-to-Hydrogen (PtH₂):** In the PtH₂ scheme, the RES-derived electric energy is converted to hydrogen, which is considered as the final product without further transformation and can ultimately be used in the industry, mobility, electricity network (including storage of excess renewables) and heating, with the industrial sector accounting for approximately 90% of the total H₂ demand. Specifically, the largest share comes from the chemicals sector for the production of ammonia and in refining for hydrocracking and fuel hydro-treating processes. Other industrial sectors include the production of iron/steel, electronics, glass, bulk and specialty chemicals, but their combined share in the global demand is not high [17,203].

Through PtH₂, renewable electrolytic hydrogen has the potential to transfer high loads of renewable electric energy to sectors for which decarbonization is otherwise difficult or even unfeasible. Specifically, aside from the obvious benefit of partial or even complete replacement of the fossil fuel-based hydrogen to meet the demands of the industrial sector (provided that PtH₂ attains economic competitiveness), Power-to-Hydrogen can offer significant advantages in other sectors. Most notably, hydrogen can be potentially injected into the existing natural gas grid up to a certain threshold, thereby reducing the overall demands and increasing the environmental impact of district heating [204,205]. An additional advantage of this is the fact that hydrogen can be stored on a relatively large scale and for longer period compared to other means of energy storage, enabling the coping of the system with the inevitable variations in demand and allowing for an inter-seasonal storage capacity for meeting seasonal peaks in demand (e.g., increased heat loads during the cold season) [17]. Another field that can be benefited is the transport sector, since fuel-cell electric vehicles can be considered as a zero-carbon option compared with the driving performance of conventional vehicles in terms of both driving range and refueling time and can act as complementary to battery electric vehicles [206,207].

Lastly, an extension of PtH₂ is the Power-to-Power scheme, in which stored H₂ is subsequently reconverted into electricity and heat through a fuel cell (i.e., reverse electrolysis). Through optimal planning of RES with short and long-term storage capacity, this can mean avoiding energy-related CO₂ emissions when an adequate RES supply cannot be provided. It must be stated, however, that a significant obstacle towards the implementation of PtH₂

applications is the absence of a dedicated means for hydrogen storage and distribution infrastructure, as opposed to natural gas [208].

Moreover, the applicability of the aforementioned Power-to-X schemes has been extensively studied in the literature, as PtX schemes have been attracting increasing scientific attraction over the last decades. Since PtX is not by any means a monolithic scheme limited to a certain scale and confined within the boundaries of a single physical or chemical process, its evaluation requires a wide array of disciplines, ranging from lab-scale efforts (e.g., catalysts, electrochemistry) to real-world deployments (e.g., feasibility and sustainability assessments, legal and standardization framework). These issues have been addressed in recent works examining PtX through a holistic/macroscopic approach [201,209–211].

In this regard, aside from the extensive research that has been conducted on the appropriate materials for catalyzing the respective CO₂ hydrogenation reaction, various works have assessed PtX from a techno-economic or environmental viewpoint. In general, although an overall conclusion cannot be unequivocally reached due to the case-specific nature of any such study, promising results have been obtained for PtX implementation at a wide scale range and based on a variety of CO₂ hydrogenation products, such as methanol [212–214], DME [215–217], liquid hydrocarbons [218–224] or light olefins [225,226]. Additionally, a comparison of these routes has been made in the recent review by Dieterich et al. [202] and in the work by Atspha et al. [220]. Furthermore, a plethora of works examine the environmental sustainability of PtX through a life cycle assessment (LCA) methodology (see [209,227–231] and references therein). Last but not least, and as an extension of the voluminous literature works examining PtX from a theoretical standpoint, it needs to be highlighted that PtX is by no means a nascent scheme, evidenced by the number of pilot and/or demonstration projects already operating or that are under development throughout the world, as reviewed extensively in [232–235].

In all, even though a variety of PtX routes have been gaining attention, the production of synthetic natural gas (SNG) via the so-called “Power-to-Gas” scheme dominates the relevant literature, as well as the number of PtX pilot projects. The various benefits that can be obtained by the production of SNG from CO₂ hydrogenation largely stem from the augmented modularity of Power-to-Gas compared to the other Power-to-X routes [236,237]. Moreover, owing to the already mentioned recent energy crisis which has affected natural gas availability and pricing worldwide, the development of large-scale synthetic natural gas production may attract even more attention and resources in the short term. Therefore, the process of Power-to-Gas is described in more detail in the following dedicated section. Finally, it must be underlined here that the term “Power-to-Gas” (also abbreviated as PtG) is used interchangeably in the literature and refers to the storage of excess energy from RES in a chemical form of gaseous substances, mainly hydrogen or methane, aptly called Power-to-Hydrogen (PtH₂) or Power-to-Methane (PtM) processes. However, for the purposes of this review, the terms “Power-to-Gas” and “PtG” will be henceforth used to denote the Power-to-Methane scheme.

7. Power-to-Gas

7.1. Brief Overview

Historically, the Power-to-Gas concept was first proposed by Koji Hashimoto in 1994 [238], although processes involving the reaction of CO₂ methanation were under development for more than a century (Figure 14). Essentially, PtG refers to the already mentioned coupling of the storage of surplus renewable energy using gaseous H₂ as the energy vector and the capturing of CO₂ emissions in order to convert both into a mixture consisting predominantly of methane, i.e., SNG. The most significant advantage in opting for generating SNG as an end product in this specific Power-to-X process is the fact that SNG can be injected into the existing grid or gas storage system, used as compressed (CNG) or liquified (LNG) natural gas motor fuel or be easily utilized in the well-established and widely-located natural gas facilities worldwide, such as district heating (Figure 15) [233]. Indicatively, it is projected that the global natural gas vehicle market share will attain a

value of around 10% until 2050 [239]. In this way, the process is largely decoupled from the issues arising from the distribution and storage of the final product in PtL and PtH₂ schemes, for instance, as the existing natural gas infrastructure has been used for many decades in many countries and has been largely optimized in terms of cost and safety issues for transportation in short, medium and high distances.

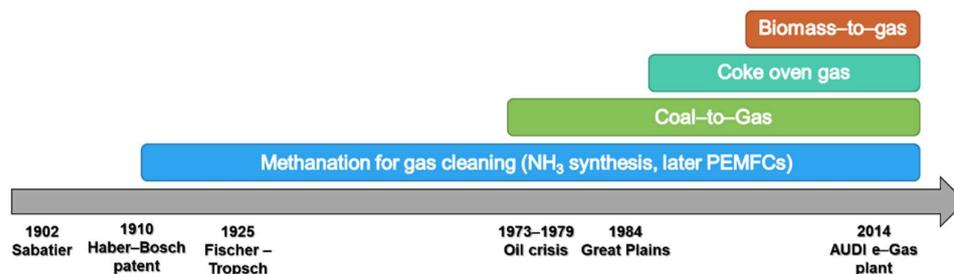


Figure 14. Timeline of the uses of the reaction of CO₂ methanation. Adapted from [240].

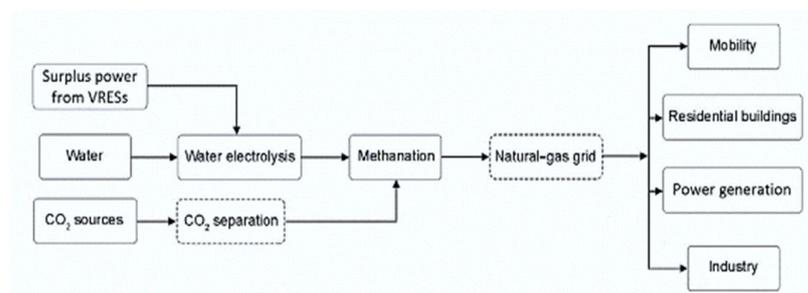


Figure 15. The basic concept of Power-to-Methane. Reprinted with permission from [232].

The physicochemical properties of SNG and conventional natural gas are in theory very similar, to the point that practically neither technical changes in the end systems nor new investments in the storage, transport and utilization infrastructures are deemed necessary. Therefore, an injection of very high volumetric flows of SNG into the natural gas grid is possible. Adding to the obvious financial benefits, this is also time-saving regarding authorization and also beneficial from a general public acceptance viewpoint, an often-crucial bottleneck for the deployment of new projects. Ergo, given that natural gas is used in a variety of industrial facilities either as primary or secondary fuel due to its availability and improved combustion characteristics combined with reduced CO₂ emissions compared to other fossil fuels, large-scale production of SNG will lead to minor or non-existent retrofitting issues and partly or completely negate the need for replacement of natural gas with cleaner alternatives and the associated costs in many industries. Nonetheless, PtG is yet at a TRL level of 5–7 and further research is required in order to decrease investment costs and fully evaluate its environmental impact.

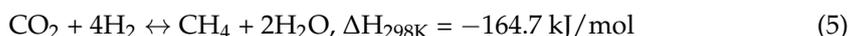
All the above points further towards the fact that the coupling of a CO₂ methanation unit with a RES-powered hydrogen production unit is almost imperative. Indeed, it has been estimated that under a scenario of 85% RES penetration in the German energy mix, PtG combined with other storage technologies could effectively calibrate the surplus energy by the variable renewables, making PtG a valid option at high renewable shares [241]. In principle, although the operation of a PtG plant can be entirely supplied by RES, it could alternatively be grid-connected, operate continuously, only in times of surplus electricity or even when electricity prices are low.

Along with the curtailment of intermittent RES energy, Power-to-Gas systems can potentially offer several advantages to the energy system as a whole [242]. Importantly, PtG systems can be used for load balance in a large-scale energy system when the percentage of RES load output is high, since the balancing of the load via the use of conventional power sources is not an easy task [243]. In other words, PtG can provide flexibility to an energy

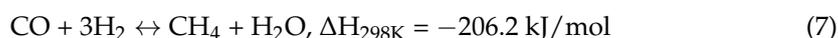
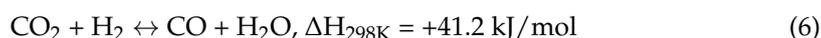
system and increase its ability for a continuous operation irrespective of the unpredictable and rapid changes in the supply/demand balance of RES-based energy, as energy balancing currently lies largely on the supply side. This is showcased by the fast response time, which is usually several seconds or minutes, depending on the technology of electrolysis. Notably, Power-to-Gas systems enable the integration of all important energy sectors (gas, electricity, heat and even the CO₂ market) in one interconnected system [158]. It can be expected that in such configurations the balance would lie between both supply/demand and among the different networks. Another role of PtG might potentially be the conversion of the electric energy generated in remote locations into SNG and subsequently the use of the existing grid for energy transport and distribution to consumers, although its efficiency is deemed to be low [244,245]. Additionally, compared to biofuels production, it has been demonstrated that Power-to-Gas is more sustainable in terms of land requirement and water consumption [246].

7.2. Thermochemical CO₂ Methanation

The hydrogenation of carbon dioxide into methane is also known as the Sabatier reaction, since its discovery in 1902 by Paul Sabatier and proceeds via the following chemical equation (Equation (5));



CO₂ methanation is thought to be the equivalent of two processes, the endothermic reverse water-gas shift (rWGS) reaction (Equation (6)) and the highly exothermic CO methanation (Equation (7)). In other words, methane is produced by the intermediate step of CO formation, albeit the reaction mechanism is still not fully elucidated and is catalyst-dependent. It can also be inferred from Le Chatelier's principle that CO₂ methanation is thermodynamically favored under low temperature and high pressure, due to its exothermic nature and mole-reducing, respectively (see Figure 11). However, a low reaction temperature significantly hinders the reaction kinetics and necessitates the use of an appropriate catalyst, whereas at the same time CO_x hydrogenation reactions are highly exothermic, thus high reaction temperatures will limit reactants conversion. Additionally, the Sabatier reaction is an eight-electron process, associated with the complete reduction of the carbon atom from +4 (in CO₂) to −4 (in CH₄), evidenced by the differences in the Gibbs formation energy between CO₂ (−395 kJ/mol) and CH₄ (−51 kJ/mol).



The effluent composition can be influenced by several factors, mainly the reaction parameters (temperature, pressure, H₂:CO:CO₂ ratio) and reactor configuration [247]. Additionally, the employed catalyst influences the reaction kinetics, conversion and products distribution [137,143,178,248]. From a process system perspective, the input stream to the reactor has to meet some requirements in order to avoid catalyst poisoning (e.g., due to the presence of tar, NO_x or chlorine species), unnecessarily high reactor volume (due to non-negligible amount of inert N₂) or side reactions and demanding purification steps for O₂ removal [208]. Additionally, at the reactor outlet, in addition to methane, the gas consists typically of unconverted CO₂ and H₂, large amounts of H₂O, CO formed by rWGS, as well as unconverted educts (usually NO_x, SO_x or N₂). A typical operation window for the industrially implemented CO₂ methanation reaction is 250–550 °C and 10–50 bar [160,208].

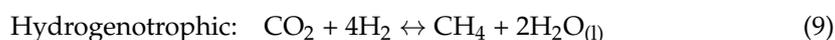
Given the above, a major issue towards PtG implementation is the heat management from the largely exothermic reaction involved. Indicatively, Götz et al. [160] have estimated that, for CO₂ methanation, around 2 MW_{th} per cubic meter of the catalyst bed need to be removed whereas the corresponding value for methanol synthesis was significantly lower, i.e., 0.6 MW_{th}/m³. Consequently, the realization of adequate temperature control

in the reactor system in order to overcome the thermodynamic limitations and catalyst thermal aging (sintering) is of utmost importance. Regardless of the selected reactor design, however, the reaction heat has to be continuously removed. To this end, several reactor configurations are currently implemented for large-scale Power-to-Gas plants that need to be optimized for proper heat management and operation under intermittent and/or dynamic conditions.

Lastly, in the scheme of RES energy to SNG, another differentiating parameter needs to be mentioned. Specifically, the reactor may operate under either steady-state or dynamic conditions, according to RES intermittency. For the latter, a high-capacity hydrogen storage is required in order to ensure a constant flow of hydrogen to the methanation reactor, assuming that CO₂ flow is also constant from the capture unit. However, it is inevitable that this increases the PtG facility costs [156]. On the other hand, dynamic operation changes significantly the requirements for the catalytic material and reactor design. One important issue is the challenging matter of operating the reactor in stand-by mode, during which a hydrogen atmosphere upon the catalyst would be advantageous for prolonging catalyst lifetime. Equally importantly, large variabilities in the reactor temperature under dynamic operation may arise if the response time for the reactor cooling is not sufficiently low, eventually leading to catalyst deactivation via cracking or sintering due to the high temperature gradients [160].

7.3. Biological CO₂ Methanation

Biological methanation (or bio-methanation) is another option for the PtG process, using methanogenic microorganisms as catalysts for the reaction, producing the necessary enzymes. Bio-methanation is established in biogas processes, where two main methanogenesis paths are known to occur, described by Equations (8) and (9);



Evidently, Equation (9) is equivalent to Equation (5), with the exception that water is released mostly in liquid form (vapor fraction is about 2% at the operating conditions), thus releasing more heat than thermochemical methanation which produces solely water vapor, due to the latent vaporization heat [249]. Additionally, both metabolic pathways are catalyzed by different microbes [208]. The acetoclastic route is the dominant process for biomass decomposition, whereas hydrogenotrophic methanogenesis is employed in biogas plants with a mixed microbe population. The activity of the methanogenic archaea is temperature-dependent and generally takes place at 1 bar and at 0–122 °C, with the optimal temperature ranging between 15–20 °C and 70–90 °C, depending on the micro-organism used [250].

The largest group of methanogenic organisms are the so-called autotrophic hydrogenotrophic methanogens [251], thus this process can be effectively be performed in a typical biogas plant. Such a plant involves firstly biomass hydrolysis to simpler compounds (monomer compounds such as mono-saccharides, amino acids, and fatty acids). Subsequently, monomers are converted to a mixture of acetate, CO₂ and H₂, in what is called acidogenesis and acetogenesis. Lastly, CH₄ is generated via the depletion of acetate and the reduction of CO₂ with H₂ [252]. The required energy for the growth of micro-organisms is provided by the anaerobic metabolizing of CO₂ and H₂. Biological methanation is considered less promising from a catalysis standpoint, due to numerous challenges arising from its non-flexible and complex nature, extremely slow kinetics and substantial mass transfer limitations. Biological methanation may take place either in situ in digester or ex situ in a separate reactor. In general, three designs have gained technological maturity so far, offering both satisfactory conversion efficiency and enlargement capability [251]:

- Continuously Stirred Tank Reactors;
- Fixed-Bed Reactors or Anaerobic Filters;

- Trickle-Bed Reactors.

Collectively, the two aforementioned processes for CO₂ methanation are comparatively assessed in Table 5, adapting data from previous works [160,208]. It becomes apparent that each concept is characterized by both advantages and disadvantages, thus the decision for employing a process requires a balance of their pros and cons and most certainly further research and development. Finally, an overview of the current status of Power-to-Gas plants worldwide, projections for future deployment [157,196,208,233,253,254], as well as life-cycle assessments [227,255] can be found in dedicated review papers and are not discussed here.

Table 5. Comparison of thermochemical and biological methanation in terms of process design parameters. Adapted from [208].

Process Parameter	Chemical Methanation			Biological Methanation
	Fixed bed	Fluidized bed	Bubble (slurry)	
Heat release	Very poor	Good	Very good	Very good
Heat control	Very poor	Average	Very good	Very good
Mass transfer	Average	Very good	Very poor	Very poor
Kinetics	Good	Good	Good	Average
Load flexibility	Average	Very poor	Average	Very poor
Catalyst stress	Good	Very poor	Good	Very good

8. Conclusions and Outlooks

By now, it has been established in the scientific community as well as in the general public throughout the world that the global warming effects induced by increasing greenhouse gases (and predominantly CO₂) emissions in the atmosphere are a rather grim reality and can be potentially life-threatening for many societies scattered around the globe. In this regard, numerous reports have systematically showcased that the past and present rates of fossil fuel consumption are responsible for a wide array of changes in the climate of our planet. Nonetheless, it is highlighted that this is not necessarily unavoidable or even irreversible, provided that immediate action is taken at a global level towards the establishment of carbon neutrality. Indeed, the large-scale penetration of renewable energy sources can substantially decrease the dependence on carbon-based fossil fuels and exploit free energy sources that have the potential to meet energy demands on a global scale and would otherwise be wasted, effectively diversifying the future energy mix. Even more importantly and provided that not all sectors of the increasingly industrialized society can be successfully decarbonized or fully electrified in the short-to-medium term or even ever, the implementation of large-scale means of unavoidable CO₂ emissions mitigation is deemed as an imperative.

Advancing from the above, the so-called Carbon Capture and Utilization (CCU) processes have been gaining more ground recently and can be thought of as an extension to the alternatively proposed Carbon Capture and Storage (CCS) process, the latter dealing with the large-scale deposition and storage of captured CO₂ instead of its direct utilization. Additionally, given that a large family of chemical compounds (either C₁ or C₂₊) can be potentially derived from the CO₂ molecule via its reaction with a highly energetic co-reactant such as hydrogen, it can be reasoned that this process is associated with a rather high versatility and adaptability in different applications, from well-established and widely implemented sectors such as the methanol industry or natural gas network to niche markets such as fine chemical and aromatics industry. Even more importantly, considering that large-scale electricity storage technologies are yet to be technologically mature and are thus far from meeting sustainability and feasibility targets, the full potential of the process of CO₂ hydrogenation can be realized in an integrated overall route. Specifically, not only are CO₂ emissions valorized by being transformed into forms of energy or even added-value chemicals, but at the same time the exploitation of the excess renewable energy that is

inherently produced in an intermittent manner from solar or wind energy as a source for the mass production of H₂ from water electrolysis is realized, effectively storing it in a stable and consistent manner.

Moreover, the full implementation of industrial CO₂ hydrogenation is still undergoing optimization in terms of catalyst tuning, process system design and/or integration with existing units and sectors and has not reached a sufficiently high TRL value. Since this scheme is essentially based on the constant influx of large amounts of both CO₂ and H₂, it becomes obvious that their provision must be optimized and not be considered a bottleneck. Although direct capture of carbon dioxide from the air is theoretically possible, its application is limited so far due to infeasibility and efficiency issues. In this regard, appropriate sources of CO₂ are needed, with the capture of CO₂ from the flue gases of large industrial units that cannot be practically decarbonized, such as cement or iron/steel factories or even natural gas power plants, which are the most promising candidates. These sectors emit very large amounts of CO₂ annually, both flow- and fraction-wise. Thus, a substantial decrease or even complete negation of their carbon footprint would act by itself as a great incentive for investments in retrofitting post-combustion capture technologies of emitted CO₂, let alone the additional economic benefits that can potentially arise through the eventual market exploitation of highly valued chemicals or even synthetic fuels that can be derived from the captured carbon dioxide. As for hydrogen, it is rather obvious that conventional H₂ production via natural gas steam reforming makes no environmental sense in terms of CO₂ valorization via hydrogenation. To this end, the total needs for hydrogen supply must be met by environmentally friendly sources, such as biomass gasification or solar/wind water electrolysis, providing in the latter case the additional benefit of curtailing intermittent electricity generation and stabilizing the energy mix.

In addition, there are several other issues aside from technicalities that are crucial for the large-scale implementation of CO₂ hydrogenation, or any CCS/CCU scheme for that matter. Specifically, although infusion of investments in renewable energy by governmental funds is certainly a prerequisite, the removal of financial barriers and the setting in motion of effective measures for the acceleration of both CCS/CCUS retrofitting and newly created projects which will drive continued innovation and cost efficiencies need to be also deemed as imperative. Indeed, large-scale infrastructure projects such as the one required for globally implemented CCS/CCU are inherently and practically capital-intensive, associated with design and construction costs lying most probably in the hundreds of millions, sometimes billions, of US dollars. In this regard, it is obviously more preferable for private companies to invest in projects where there is a large capital injection from government through direct grant funding, in order to support private sector equity investments. Additionally, since most of the world's liquidity is essentially locked inside the private sector, another challenge is to incentivize banks and institutions to invest in CCUS projects. In practice, measures such as the introduction of a price on CO₂ emissions reductions, (e.g., through a carbon tax, tax credit, emissions trading scheme, CCS obligation, emissions performance standard or through government procurement standards) may enable investments in facilities which can then pass on transfer of their turnover to transportation and storage providers. Additionally, through the provision of capital support, the development of shared transport and storage networks with a focus on integrated hubs and clusters can be enabled. In turn, economies of scale can potentially reduce unit costs and a diversified source of emissions can reduce the risk of asset stranding. Moreover, there is general agreement between public- and private-sector stakeholders that the absence of CCS-specific law and regulation is a critical barrier to the deployment of CCS projects in many regions.

Lastly, it should be noted that countries with limited potential for CO₂ storage are investigating the transport and storage to other nations, rendering the establishment of greater intranational collaborations critical. This has led to renewed interest in considering and addressing legal barriers to trans-boundary CO₂ movement and storage, respecting relevant domestic laws and regulations, as well as the London Protocol. The latter is an international agreement that governs waste dumping for the protection of marine environments.

In all, it can be reasoned that one of the most promising aspects of hydrogenation of CO_2 is the production of synthetic natural gas. Indeed, the production of SNG, a gas consisting predominantly of CH_4 is very attractive, especially considering the characterization of natural gas as a transition fuel towards the establishment of a carbon-free future energy mix. To this end, this process has already reached a TRL of 7 and is expected to be more widely implemented, since it provides a great way of stabilizing the energy mix through the curtailment of highly variable RES-derived electricity into a reliable energy carrier such as methane. The major advantage of this process is that its end product can be directly injected to the already existing natural gas pipeline network, which has been continuously extended in many regions in the world for decades now and is well established in terms of material and safety issues. Notably, given the expected large shares of renewable energy sources in the future energy mix, research efforts are being made towards the design of future or already existing natural gas systems for their operation with a mixture of CH_4/H_2 (sometimes referred to as hythane) with increasing H_2 content depending on the application. Thus, if a rather high tolerance (for example, 20–30 % *v/v* H_2 or even higher) can be successfully applied in the future, costly hydrogen purification needs (via either pressure swing adsorption or membrane technology) will be greatly reduced, since the unconverted H_2 can be also considered as a co-product along with the generated CH_4 .

However, no technology is free of challenges and drawbacks and CO_2 hydrogenation is no exception. In this sense, the advancement of electrolyzer technologies in the GW or even TW-scale globally is required in order to fully exploit the vast amounts of surplus RES-based electricity that are expected to be produced in the coming decades, by considering the accelerated installation of solar and wind parks worldwide, driven by reduced prices via learning curves and economies of scale. To date, this order of magnitude for water electrolysis cannot be materialized and substantial leaps in various aspects of this technology need to be made for the full-scale implementation of sustainable and economically feasible electrolyzer units. In addition, although the technology for the capture of CO_2 from a variety of industrial streams with the use of amines has been implemented for several decades, its wider deployment will require the handling of even more diverse streams in terms of CO_2 concentration and absolute CO_2 flow rates, even in the range of a few ppm to more than 30% *v/v* CO_2 and between tens of moles and a few thousand kilomoles per hour, respectively. Several alternatives to amine adsorption do exist (e.g., calcium looping or mineralization), but they have yet to reach comparable technological maturity and their sustainability is still questionable. Thus, significant research efforts need to be employed in order to integrate a reliable and effective array of CO_2 capture technologies from industrial point sources.

Collectively, it can be postulated that CO_2 hydrogenation can potentially provide a promising route of simultaneously tackling two of the most challenging issues of our era, i.e.,

- Deceleration and crucially reversion of the greenhouse effect caused predominantly by increased emissions of carbon dioxide and in turn the necessity for worldwide phasing out of carbon-based fossil fuels.
- Curtailment of large amounts of surplus electricity generated by inherently intermittent renewable sources, i.e., solar and wind.

Essentially, provided that feasible and sustainable solutions can be applied to the current bottlenecks for large-scale industrial implementation of CO_2 hydrogenation on a global level, this scheme can be adapted for a lot of applications ranging from platform chemicals to production of synthetic fuels. In this way, the gigantic task of complete industry decarbonization may not be required in the sense of climate change, as the carbonaceous energy content from the otherwise emitted CO_2 can be successfully captured and be transformed into a multitude of compounds, effectively being recycled in an ideally closed loop with minimal or practically zero carbon footprint.

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